

## VINEGAR ITS MANUFACTURE AND EXAMINATION

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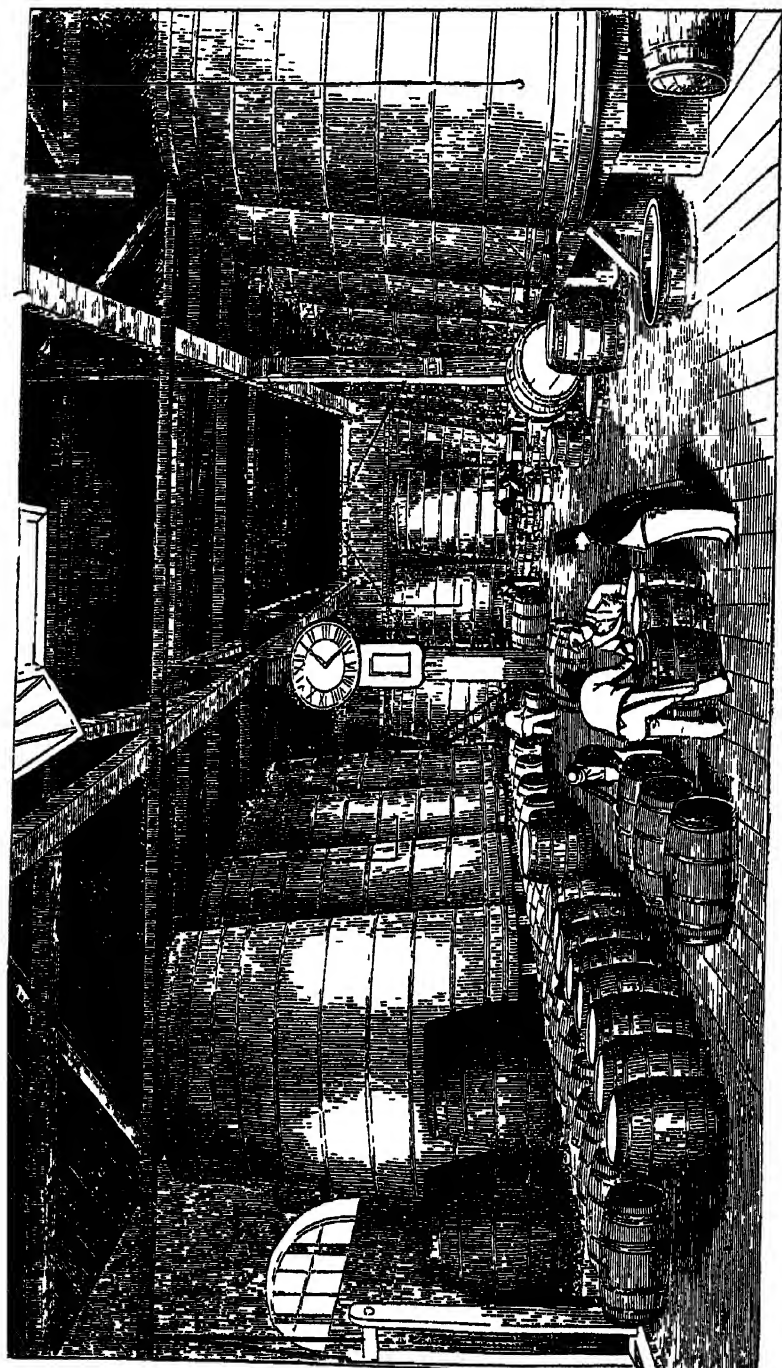
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"Neither *Vinegar*, nor any other Acids are proper for melancholy Persons, because they mix the Humours too much. They also turn those who take much of them lean, for they give too great Consistency to the Blood, and do hinder the Chyle from distributing itself sufficiently through the Body to give Nourishment"

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\* *Arcana Fairfaxiana*, 1890.





"Sending out Warehouse—Beaufoy's Vinegar Works in 1812



# VINEGAR:

## ITS MANUFACTURE AND EXAMINATION.

BY

C AINSWORTH MITCHELL, BA (OXON), FIC,

*Chemist to Messrs Beaufoy & Co, Manufacturers of Vinegar  
for nearly 200 years*

*With 5 Plates and 49 other Illustrations*



LONDON  
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1916

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In recognition of numerous kindnesses over a  
period-of many years,

**This Book is Dedicated**

to the oldest firm in the Vinegar Industry,

**MESSRS BEAUFOY & COMPANY**



## P R E F A C E

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CONSIDERING the age of the vinegar industry in this country, it is strange that no book has yet been published dealing with the subject from the English point of view. This is partly due to the fact that until a comparatively recent date the manufacture of vinegar was regarded as a mysterious process, all details of which had to be jealously guarded, not only from the outside world, but also, as far as possible, from the workmen in the factory itself. Even at the present day this tradition of secrecy is not quite dead, although the general principles of the manufacture are now common property.

The information in chemical dictionaries has been mainly derived from American, French, and German books, which in some respects are obsolete, and in any case do not embody the experience of writers acquainted with the conditions of acetification in England.

At the request of the Publishers I have attempted to fill this gap, and have tried to make clear the scientific principles underlying each stage of the manufacture, and to indicate the lines upon which development of the industry is possible.

In the analytical portion of the book I have assumed that the reader will have a general knowledge of analytical

chemistry, and have omitted details to be found in any ordinary text-book With regard to the interpretation of analytical results, I have laid stress on the present unsatisfactory state of the law, and have pointed out the difficulties which this uncertainty causes both to the manufacturer and to the public analyst

It gives me great pleasure to acknowledge the assistance I have had from various friends in writing the book, and in particular I would thank Messrs Beaufoy & Co and Major Hamilton Pott for allowing me to use historical and other material in their possession

I have also to acknowledge my indebtedness to Messrs. Pontifex & Co for the loan of blocks illustrating machinery made by them

My best thanks are also due to Miss M B Ellhott for the help she has given me in reading the proofs

C A M

WHITE COTTAGE,  
THE COMMON,  
AMERSHAM,  
BUCKINGHAMSHIRE

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# VINEGAR





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### CHAPTER I

#### HISTORICAL INTRODUCTION.

Early Scientific Views   Vinegar in Alchemy and Iatro-Chemistry—Domestic Manufacture—Early Manufacturing Processes—Alegar—Vinegar Manufacturers—Legislation on Vinegar—Proof Vinegar—The Acetometer—Trade Numbers of Vinegar

**Vinegar in Alchemy and Early Chemistry.**—Passing over various allusions in the Classics to *Acetum*, and the fable of its use by Hannibal to dissolve the Alps, we find that vinegar had its recognised place among the products of the alchemist, and was indicated by the symbols  and , while for distilled vinegar the characters  and  were used. These symbols were retained after the transition of alchymy into what has been termed “iatro-chymistry,” from its being mainly concerned with the action of different bodies upon the human system. The doctrines of the alchemists were discarded but slowly, and we find that even at the beginning of the eighteenth century all natural things were held to consist of the five principles—Spirit, Oil, and Salt (which were active), and Water and Earth (which were passive)

According to Lemery,\* there were three sorts of liquors known as *Spirit*, the *Spirit of Animals*, the *Burning Spirit of Vegetables*, and the *Acid Spirit*. The first was typified by Spirit of Hartshorn, the second by Spirit of Wine, while the last, as "the Spirit of Vinegar, Tartar, and Vitriol, is an Acid Essential Salt, dissolved and put in fusion by the fire, as I shall prove when I speak of Vinegar." †

In discussing the nature of vinegar, Lemery remarks — "Wines like other Liquors that use to ferment do grow sower by the Dissolution of their Tartar in a second fermentation. This Dissolution is commonly made, when upon the Wines going to decay, some of the more subtle Spirits are lost, for the Tartar taking their Place, fixes the rest of the Spirits which remain in the Wine, so that they can act no longer. This Fixation is the Cause that when the Wine turns sower, very little quantity of it is diminished, and very little Tartar is found in the Vessels wherein *Vinegar* is made

"To the End that Wine may quickly sower, you must set the Vessel that contains it in some hot Place, and mix the Lees from Time to Time, for this Tartar will easily dissolve when Heat comes to act upon it" . . . "The Acids (in Vinegar) continue a long Time, but being moved and continually agitated by the Sulphurs which intangled them, they at last evaporate into the Air, and so the strongest *Vinegar* by length of Time becomes almost insipid."

The following passage is of interest, since it throws

\* *A Course of Chymistry* (4th English edition from 11th French edition), 1720, p. 6

† *Ibid*, p. 404.

light upon the term ‘*radical*’ vinegar, which survived into the last century,\* and also shows that a concentrated acetic acid was prepared from distilled vinegar by neutralisation, concentration, and redistillation, as far back as the seventeenth century — ‘Some having dried and calcined the sweet Extract that remains at the bottom of the Cucurbit, after the Distillation of *Vinegar*, and having by Solution, Filtration and Coagulation, separated from it an Alkali fixt Salt, much like to that which is

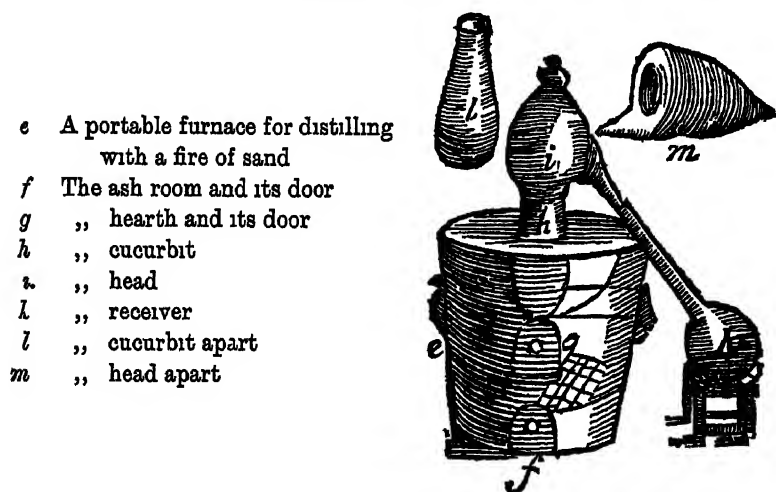


Fig 1 —Early Apparatus for Distilling Vinegar

drawn from Tartar, they mix it with *Spirit of Vinegar*, and distil and cohobate it divers Times, until, say they, the Spirit has carried off all the Salt, and then will needs have it called *Spirit of Vinegar Alkalized*, or *Radical Spirit of Vinegar*, and they affirm that this being much more pure and entirely united with its proper Salt, is much the more powerful in dissolving Metals ”

In the directions given by Lemery for the distillation

\* See the Act of George III. of 1818, p 12.

of vinegar, the liquid is first evaporated in an earthenware basin on a hot-water bath, until a sixth part, "which is the plegmatic Part," is expelled. The remainder is then "poured into a glass or earthenware Cucurbit and distilled in a strong Sand-heat, until there remains at Bottom nothing but a Substance like Honey."

"This *Spirit of Vinegar*," he adds, "is mixed in Cordial Potions to resist Putrefaction. It is mixed with Water, and this *Oxyerate* is used to stop Hemorrhagies taken inwardly, and to assuage Inflammations applied outwardly."

"Neither *Vinegar*, nor any other Acids are proper for melancholy Persons, because they mix the Humours too much. They also turn those who take much of them lean, for they give too great Consistency to the Blood, and do hinder the Chyle from distributing itself sufficiently through the Body to give Nourishment."

**Domestic Manufacture.**—Long before any vinegar maker was established in this country wine vinegar appears to have been imported from France. In that strange collection of domestic recipes handed down from generation to generation in the Fairfax family, and published in facsimile by Weddell,\* there is one relating to the preparation of "Sirrupp of Viniger" in handwriting which appears to belong to the time of Queen Elizabeth. In this recipe the principal constituent is "white wine viniger," and as no directions are given for making it, such as those for the brewing of beer and cowslip wine, the making of simples for warding off the plague and curing the bite of a mad dog, or the preparation of baths for melancholy, it seems fair to infer that vinegar

\* *Arcana Parfumanaria*, 1890.



was not made in that household at all events Not until the eighteenth century (judging by the writing) do we find an entry in the index relating to the making of vinegar, and the recipe corresponding to this is not to be found in the body of the manuscript

The process of brewing home-made vinegar was probably very similar to that described by Mackenzie,\* in the following words —

‘ To every gallon of water put a lb of coarse Lisbon sugar, let the mixture be boiled and skimmed as long as any scum arises Then let it be poured into proper vessels, and when it is as cool as beer, when worked, let a warm toast rubbed over with yeast be put into it Let it work about twenty-four hours, and then put it into an iron hooped cask, fixed either near a constant fire, or where the summer sun shines the greater part of the day, in this situation it should not be closely stopped up, but a tile or something similar should be laid on the bung hole, to keep out the dust and insects At the end of about three months (sometimes less) it will be clear and fit for use, and may be bottled off The longer it is kept after it is bottled, the better it will be. If the bottle containing the liquor is to be exposed to the sun’s heat, the best time to begin making it is in the month of April ”

**Early Manufacturing Processes.**—The earliest description of a process of making vinegar appears to be that published in 1670 in the Transactions of the Royal Society under the heading “The Way of Making Vinegar in France Communicated to the Publisher by an In-

\* *One Thousand Processes of Manufacture*, 1828.

genious Physician of that Nation, living at a Place where much of it is Made " \*

Since this account throws light upon the origin of terms used to this day in the English vinegar industry, and disposes of the claim that Boerhave originated the process here described, it deserves quotation at length —

"They take two great Casks, within each of which they put at the bottom a Trevet, which must be one foot high and as large, as the largness of the Cask permits Upon this Trevet they put Vine twiggs, whereon they lay a substance called *Rape*, with which they fill both vessels within half a foot from the top This Rape is nothing else but the wood or stalks of the Clusters of Grapes The Trevet and the Vine branches are put at the bottom of the Casks, only to keep the Rape from setting at the bottom It is this Rape which alone heats and sows the Wine The two Vessels being almost quite filled with the Rape, one of them is filled up with Wine, and the other only half full for the time, and every day they draw by a Cock half the Wine that is in the full vessel, therewith quite to fill up the other, that is but half full, observing enterchangeable turns of filling and unfilling the vessels Ordinarily at the end of two or three days the half filled vessel begins to heat, and this heat augments for several dayes successively, continuing to do so till the Vinegar is perfectly made, and the workmen know that the Vinegar is made by the ceasing of the heat In summer it is a work of fifteen dayes, in winter it proceeds more slowly, and that according to the degree of Cold weather The full vessel

\* *Phil Trans Roy Soc*, 1670, vol v., p 2002

is quite open at the top, but a wooden cover is put on the vessel that is but half full

“ The Wine in changing, leaves a certain grease, which sticks partly to the sides of the Cask (and *that* they take care to do clean away), *partly* to the Rape, so that if they cleanse not the Rape from it almost every year once, the Wine turns into a whitish liquor, which is neither Wine nor Vinegar In the Casks which have never served for this purpose before the Vinegar is made more slowly than in such that have been used already

“ There is no other way of keeping the Rape that hath once served already than to drown it, that is to say, to fill the vessel wherein it is with Wine or Vinegar.”

The account given by Boerhave \* of the French method of manufacturing vinegar is substantially the same as this version of 1670, and there seems to be little doubt but that many English manufacturers derived their information from one or other of these sources

**Alegar.**—The English being a beer-drinking nation, it was to be expected that the development of the vinegar industry in this country should have come by way of beer rather than of wine By analogy the product derived from beer became known as “alegar,” which stood in the same relation to ale as vinegar to wine

Boorde † in the year 1542 refers to both products in his “dyetary,” where he speaks of “Soure and Tarte Thynges as Venegre and Aleger ”

The distinction between the two products was pointed

\* *A New Method of Chemistry* by Boerhave English translation by Peter Shaw, 1753, vol II, p 129

† *First Booke of Introduction of Knowledge* (edn of 1870), vol xxxiv, p 296.

out by Cogan \* in 1586, in a passage upon the making of vinegar, where he remarks —“ Some make it of Ale onely but that is rather Aliger than Viniger ”

The term ‘alegar’ is still to be found in glossaries of local words, but is probably now practically as obsolete as is the old home-made product obtained by adding a “vinegar plant” to sour beer

The vinegar manufacturer evolved out of the brewer, for the production of vinegar was the obvious way of disposing of sour beer whether in the household or the brewery

It is probable that the earliest English products were nothing more than ale partially converted into vinegar by long exposure to the air. Subsequently the French methods of manufacture were adopted and “wash” was specifically brewed for the purpose

**Vinegar Manufacturers.**—In the Revenue Act of Charles II (1673), the vinegar thus produced as a waste product in the “common breweries” was termed “Vinegar-Beer,” and had to pay a duty of sixpence per barrel (as against 1s 3d duty upon six-shillings’ beer).

The date of the establishment of the first vinegar factory as distinct from the “common brew-house” is uncertain, but there was undoubtedly a “vinegar yard” in Castle Street, Southwark, as far back as 1641 † This yard belonged to a man named Rush, “in whose family it remained a considerable and improving manufactory until the year 1790, when it came into the hands of the present proprietors” ‡

\* Cogan; *Haven Health*

† *History and Antiquities in the Parish of St Saviour, Southwark*, 1795

‡ Messrs Pott & Co, who already had a vinegar yard in the same parish, established in 1720. Early in the present century the firm became amalgamated with Messrs Beaufoy & Co

The only name in the Excise list of vinegar makers for 1764, which is still connected with the industry, is that of Beaufoy.

Early in the eighteenth century Mark Beaufoy, a member of the Society of Friends, established vinegar works on the site of the old Cuper's Gardens on the Surrey side of Waterloo Bridge, and within a few years they had become the third in importance in London

Pennant,\* writing in 1792, makes the following allusion to these works in his description of London —“ There is a magnificence of business in this ocean of sweets and sour, that cannot fail exciting the greatest admiration, whether we consider the number of vessels or their size The boasted tun of Heidelberg does not surpass these On first entering the yard two rise before you, covered at the top with a thatched dome, between them is a circular turret including a winding staircase, which brings you to their summits above twenty-four feet in diameter. One of these conservatories is full of sweet wine, and contains fifty-eight thousand one hundred and nine gallons of Winchester measure, its superb associate is full of vinegar to the amount of fifty-six thousand seven hundred and ninety-nine gallons ”

In 1812 the ground occupied by these works was required for the southern approach to Waterloo Bridge, and the manufacture was transferred to its present site in South Lambeth

A Report of an Excise Commission which preceded the alteration of the method of collecting the duty upon vinegar showed that up to the year 1834 there were seventy-seven thousand dealers in vinegar in Great

\* *London*, 3rd edition, p 34

Britain, every one of whom received twelve visits a year from the Excise officers. In this report it was also stated that about three million gallons of vinegar were brewed in Great Britain and Ireland, for more than half of which five firms in London were responsible.

In the year 1844 there were forty-four vinegar makers (excluding manufacturers of acetic acid), and they produced in that year 2,828,043 gallons of proof vinegar, upon which a duty of £24,745 7s 6d was paid. In the following year there were 65, but by the year 1860 the number of vinegar makers had fallen again to about 50, and they still produced about 3,000,000 gallons annually\*.

Considerable light is thrown upon the development of vinegar making in this country by a study of the successive Acts of Parliament.

**Legislation upon Vinegar.**—Although the legislation in connection with vinegar has been mainly concerned with the purposes of revenue, it yet at the same time gives many interesting details of the industry. In the year 1673, an Act of Parliament was passed (XII. Car II Cap 24) imposing a duty of 6d per gallon for every Barrel of Beer commonly called Vinegar-Beer brewed by any common Brewer in any common Brow-House, the work of inspection to be carried out by the "gagers" of beer, metheglyn, etc. Apparently the revenue suffered from the evading of this duty, for in the year 1696 (VII and VIII. Wm III C. 30) a penalty of forty shillings was imposed for every barrel of vinegar concealed from the gaugers, or sent out of the works without due notice to the Excise officers.

\* Muspratt, *Dictionary of Chemistry*, 1860, p. 36.

In the following reign, by an Act passed in 1710 (VIII Anna, C 7), the duty upon vinegar was increased to

*Vinegar Charged in London from 5<sup>th</sup> July 1763 To 5<sup>th</sup> July 1764*

Henry Bampton	1761.	11	10 <sup>2</sup>
Wm <sup>th</sup> Widdensom	1081.	7.	9 <sup>3</sup>
In <sup>o</sup> Calvert.	1152.	12	9 <sup>3</sup>
Sam Thwait	3917.	3.	12
Mark Beaufoy	1531.	4	8 <sup>4</sup>
Joseph Malsbey	1174	2	9 <sup>3</sup>
In <sup>o</sup> Gould	17.	14.	4 <sup>2</sup>
Wm <sup>th</sup> Totcomb	2	19.	0 <sup>3</sup>
Joseph Williams.	0.	2	2 <sup>4</sup>
Henry Hall.	37.	2	4
Int <sup>o</sup> Smyre	3	18.	9
Silas Belmont	57.	12.	9 <sup>3</sup>
In <sup>o</sup> Howard	3	10.	9 <sup>4</sup>
Jeffery Edwards.	1.	17.	6 <sup>3</sup>
	<u>10783.</u>	-	11 <sup>3</sup>

*Byd<sup>r</sup> Dealer* {

Fig 2.—Facsimile of Excise List of Vinegar Brewers, 1763.

9d per barrel, and remained at that rate throughout the whole of the following century

By the Act of VI Geo III C 14, it was enacted that cider and perry that had turned sour and become unfit for sale were to pay duty as vinegar, while in 1796 (XXXVI Geo III C. 72) vinegar-makers were not allowed to have a distillery upon the same premises. They were also, before obtaining a licence, obliged to declare whether they intended to make vinegar from malt or corn, or from molasses or sugar.

In 1818 (LVIII Geo III C 65) the old duties were repealed, and a duty of 4d per gallon levied upon vinegar, vinegar-beer, aleger, radical vinegar, verjuice, acetous acid, acetic acid, pyroligneous acid, and liquors intended for vinegar made in England and Ireland, and of 1s per gallon upon imported vinegar and acetic acid, with a drawback of 4d per gallon for exported products upon which the duty had been paid.

To prevent the introduction or sale of strong acetic acid upon which only the duty for "common vinegar" had been paid, it was enacted that "all such liquors shall be tried with such acetometer as may be devised by the Commissioners of Excise. If found above proof a proportional charge was to be made for the excess." "Proof" vinegar was defined in this Act as that containing "such strength of Acetous Acid that 100 parts of the Liquor by Weight shall saturate or neutralize  $14\frac{1}{2}$  parts by weight of crystallized subcarbonate of soda."\*

No foreign acid was to be added to vinegar except sulphuric acid in a proportion not exceeding one thousandth part by weight (*Sec 25*).

Moreover, no person was allowed to make vinegar

\* This corresponded to 4.74 per cent of the so-called "dry" acid.



from malt or other fermentable matter at any place used for the preparation of acetous acid

The drawback allowed by this Act, for exported vinegar upon which the duty had been paid, was subsequently, in 1821 (I and II Geo. IV. C 102), made proportional to the acetic strength as estimated by an acetometer

Four years later (VI Geo IV C 37), the excise duty upon vinegar was again altered to 16s 8d for 100 gallons, and by VI Geo IV C 81, the licence for the manufacture of vinegar was fixed at £5 per annum

In the following reign two Acts concerning vinegar were passed. In 1833 (III Gulhelm IV C 56) the customs duty was fixed at £18 18s per tun, while in 1836 (VI and VII Gulielm IV C 65) the Act of George III dealing with the collection of the excise duty was repealed so far as it concerned the retailers of vinegar. This change was made upon the report of Commissioners who estimated that the number of dealers and retailers was very large (see p. 9), and that the continual inspection of the stock was expensive and unnecessary, since the duties might be much more readily collected from the manufacturers

In 1840 (III Vict C 17) an additional charge of 5 per cent. upon the customs and excise duties upon vinegar was imposed, but four years later the excise duty upon vinegar was entirely abolished (VII. and VIII Vict. C 25), though a manufacturer's licence was still required, while the customs duty was fixed at £4 4s per tun of proof vinegar or acetic acid (VII Vict C 16) The licence for having a vinegar still or retort was fixed in 1846 at ten shillings a year (IX. and X Vict C 90)

**Proof Vinegar.**—With the repeal of the duties upon vinegar and acetic acid, the word “proof acid” became obsolete, and the acetometer, by which the strength was ascertained, became a curiosity of the past. The terms ‘proof,’ “ $\frac{P}{50}$ ,” and so on, still linger, however, in the vocabulary of the older workmen in vinegar and acetic acid works, while discarded acetometers may still survive here and there, although they have long since ceased to be made.

Since, however, they have historical interest in the vinegar industry, a brief outline may be given of the method by which the revenue officers determined the strength.

The acetometer was a particular form of hydrometer, having a silver cup to receive weights at the top of its stem. These weights were added until the hydrometer sank in the liquid to a mark made upon the stem. The acid or vinegar to be tested was first diluted with an equal volume of rain water, and neutralised by the addition of slaked lime introduced in slight excess. As considerable heat was produced by the neutralisation, the liquid was always cooled to 70° F. before testing. In the case of vinegars an extra weight marked M (“the mucilage weight”) was used to compensate for the solid matter, and the reckoning taken from the numbered weights subsequently used. The weight marked “ $\frac{10}{P}$ ” indicated the strength of the “best vinegar” freed from solid matter (“mucilage”), and was the strength fixed by the Act of George III. as “proof acid.” The 20 weight indicated twice that strength of vinegar,

the 30 weight three times the strength, and so on up to 80, which corresponded to 35 per cent over proof, or the strongest acid upon which duty was charged by means of this instrument. There were also three intermediate weights, 8, 4, 2, and two fractional weights, 1 and  $\frac{1}{2}$ .



Fig. 3 —Obsolete Excise Acetometer.

The specific gravity of the calcium acetate solution was approximately double that of the original acid. Thus, an acid of specific gravity 1.009 showed 1.018 in the acetate solution. Vinegar of the same strength would show about 1.023, from which 0.005 would be deducted for the mucilage or extract. The proportions of acetic acid

corresponding to the acetometer strengths were thus as follows —

Acetometer,	$\frac{1}{2}$	1	2	4	8	$\frac{10}{P}$	20	30	40	50	60	70	80
Acetic acid (per cent ),	$\left. \begin{array}{l} 0 \ 25 \ 0 \ 5 \ 1 \ 2 \ 4 \ 5 \ 10 \ 15 \ 20 \ 25 \ 30 \ 35 \ 40 \end{array} \right\}$												

As a matter of fact, the strength of “proof vinegar” was only approximately 5 per cent., the neutralisation value fixed by Act of Parliament corresponding to a vinegar containing 4.74 per cent of “real” acetic acid (see pp 12, 60)

The estimations of the acidity made with this instrument were very rough, and the variations in the amounts of solid matter were so great in different vinegars that the allowance made for them by the “mucilage weight” could at best be only approximately correct

In Nicholson's *Dictionary of Chemistry* (2nd ed ), 1823, it is stated that Taylor's acetometer was based upon the following table —

REVENUE PROOF ACID, CALLED BY THE  
MANUFACTURER No 24

Sp gr	1.0085	contains real acid in 100,	5
„	1.0170	„ „	10
„	1.0257	„ „	15
„	1.0320	„ „	20
„	1.0470	„ „	30
„	1.0580	„ „	40

“The acetic acid or radical vinegar of the apothecaries, in which they dissolve a little camphor or fragrant essential oil, has a specific gravity of about 1.070 ”

**Trade Numbers of Vinegar.**—As a rule, vinegar is not

sold to the retailers in accordance with acetic strength, but is described by the numbers 16, 18, 20, 22, and 24

The origin of these numbers has been attributed to the price in pence per gallon at which the vinegar was once sold, but even in 1842 it was stated \* that " although the price no longer accords with these numbers, the numbers themselves have been retained as symbols whereby a certain quality of vinegar may be known and designated "

This explanation is borne out by Phillips' *Translation of the Pharmacopœia*, for the year 1824, where it is stated that " the strongest vinegar is termed *proof vinegar*, and by the manufacturer called No 24 It is estimated to contain 5 per cent of real acetic acid, and the maker is allowed to mix one-thousandth of its weight of sulphuric acid with it "

On p 18 of the same edition the writer makes it clear that by " real " acetic acid is meant what we now term acetic anhydride, but what was then regarded as the hypothetical " dry " acid, and he states that 50 grains of real acetic acid neutralise 153 grains of crystallised subcarbonate of soda (*i e*, crystalline sodium carbonate) Calculated upon this basis, the *proof vinegar* of the Act, or No 24 vinegar, contained 4.74 per cent of " real " acetic acid, or 5.5 per cent of acetic acid as is now understood by the term

The other explanation of the trade numbers is given by Muspratt,† who states that " proof vinegar has a specific gravity of 1.0085, and contains about 5 per cent of acetic acid In commerce this vinegar is

\* *The Penny Magazine*, 1842, p 430 The same explanation is also given in Tomlinson's *Cyclopædia of Useful Arts*, 1854, p. 7.

† *Dictionary of Chemistry*, 1860, p. 32

## 18 VINEGAR ITS MANUFACTURE AND EXAMINATION.

represented by No 24, from the fact that 24 grains of pure dry carbonate of soda are required to neutralise a fluid ounce. Weaker vinegars are represented by the Nos 18, 20, 22, according to their strength, and, as in the foregoing instance, these figures equal the number of grains of carbonate of soda that will saturate a fluid ounce."

The chief objection to this explanation is that the strength of proof vinegar was estimated according to the Act of George III., not by means of anhydrous sodium carbonate, but by neutralisation with "crystallised carbonate of soda," which corresponded to the modern crystalline sodium carbonate ( $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ ). According to this, proof vinegar contained 4.74 per cent of the hypothetical "dry" or "real" acetic acid, and not 5.27 per cent, as would be required to comply with Muspratt's explanation.

The statements in Phillips' *Translation (supra)* are conclusive upon the point, for they show that the term "No 24" was in use soon after the passing of the Act.

On the basis of this latter explanation, which was accepted by many vinegar manufacturers, the "numbers" of the different vinegars would have the following strengths in terms of "real" or "dry" acetic acid and its corresponding modern equivalent—acetic acid.

Number of Vinegar	"Dry" or "Real" Acetic Acid	Acetic Acid
	Per cent	Per cent
16	3.4	4.1
18	3.9	4.6
20	4.38	5.16
22	4.76	5.6
24	5.27	6.2

In practice there has been no uniformity upon this point among different manufacturers No 16 vinegar, for example, has been sold at strengths ranging from 3.5 to 4.2 per cent, while No. 24 has usually contained from 5.5 to 6.0 per cent of acetic acid, and has seldom been sold at a strength of 6.2 per cent

Some years ago a still weaker vinegar than No. 16 was known to the trade as 'Diamond Vinegar,' but since the recommendation of the Local Government Board as to the strength of vinegar, the sale of any vinegar weaker than 4 per cent is liable to be followed by a prosecution

## CHAPTER II

### THEORIES OF ACETIC FERMENTATION.

**Early Theories of Acetification—Liebig's Theory—Pasteur's Views—Nägeli's Mechanical Theory—Later Enzymic Theories—The Enzyme of Vinegar Bacteria—Oxidation and Reduction Processes**

**Early Theories of Acetification.**—The conditions necessary for the successful acetification of alcoholic liquids were known empirically long before it was recognised that the oxidation of alcohol into acetic acid, as practised in vinegar works, was of a process analogous to the fermentation of sugar into alcohol. Various phenomena in the manufacture of vinegar were recorded, but not until the 19th century was well advanced was there any plausible attempt to explain their significance.

For example, in 1822, Persoon made a microscopical study of the films that develop upon wine and beer when exposed to the air, and found them to be made up of cells resembling yeast cells. He gave to these pellicles the general name of *Mycoderma* (mucinous skin), but did not associate them with the development of acidity.

Berzelius, in 1829, extended his theory of catalytic action to cover the function of the "mother of vinegar" in acetification, but attributed the fermentation not to any living cell or product of a living cell, but to the



action of the acetic acid enclosed within the pores" of the mucinous skin

Then in 1837 Kützing examined the skin, and described the small cellular structures, arranged in chains, of which it was composed. He recognised that these were living organisms, and regarded them as algæ (*Uvula aceti*), by the vital activity of which alcohol was transformed into acetic acid.

**Liebig's Theory.**—In the year 1839 Liebig\* published his theory of the nature of alcoholic fermentation, and extended it to cover also the fermentation of alcohol into acetic acid. This theory had many points in common with that of Stahl (1697), for both looked upon the ferment as a body in a state of decomposition, and capable of imparting its motion to surrounding bodies. Liebig, however, included all processes of fermentation under ordinary chemical actions, and in support of his view that a small quantity of one substance could bring about changes in large quantities of other substances, cited phenomena such as the solution in nitric acid of platinum alloyed with silver, and the action of nitric oxide in the production of sulphuric acid.

In particular, the fact that platinum black could promote the oxidation of alcohol to acetic acid was regarded by Liebig as a proof that the ferment in vinegar, "the mother of vinegar," also acted purely by chemical means. The proteins composing it underwent decomposition and communicated their motion.

Liebig subsequently modified his opinion to the extent that fermentations were caused by enzymes produced within the living cells, and that the physiological growth

\* *J. prakt. Chem.*, I, 35, 312

of the cells had nothing to do with the fermentation itself, but was merely the means by which the enzyme was developed \*

In another place † he elaborates these views —

“An atom or molecule put in motion by any power whatever may communicate its own motion to another atom in contact with it

“Hydrogen, from being in contact with decaying substances, acquires the power of combining with oxygen at the common temperature

“Other inflammable gases, both simple and compound, are affected under these circumstances in exactly the same manner as hydrogen. The vapour of alcohol, for example, when in a vessel containing wood or other substances in a state of decay, absorbs oxygen from the atmosphere, and becomes transformed into aldehyde, and subsequently into acetic acid, which, upon assuming a fluid state, is withdrawn from the further influence of the oxygen

“It is upon this power of substances undergoing decay to increase the attraction of all organic substances for oxygen, and especially the affinity of alcohol for this element that a speedy process for acidifying alcohol was based, which is termed the ‘Schnellessig-fabrikation,’ or ‘quick vinegar process’

“The transformation of fermented liquors into vinegar formerly required weeks, and even months, to accomplish in consequence of the imperfect access of the air: we can now convert alcohol into vinegar in less than twenty-four hours, and this is effected mainly by making brandy

\* *Annalen der Chem u. Pharm*, 1870, cliv

† *Liebig, Letters on Chemistry*, London, 1851, p 216

diluted with water, or any other weak spirituous liquor, trickle slowly through casks filled with wood shavings, and at the same time causing a slight stream of air to circulate through these shavings

“At the commencement of this process it is usual to add to the dilute spirit a small quantity of some substance containing matter capable of undergoing the process of decay, such as beer wort, honey, vinegar, etc., but after the lapse of a very short time, the surface of the wood shavings passes into a state of oxidation, and from that moment effects the transformation of the spirit into vinegar without the further co-operation of extraneous decaying matter”

In a later paper\* Liebig expressed the opinion that the mother-of-vinegar was not essential to acetic fermentation, but that its place could be taken by dead vegetable matter “It is unquestionable,” he says, “that mother-of-vinegar is capable of effecting the oxidation of alcohol into acetic acid, but this action does not depend upon a physiological process Alcohol requires for its conversion into acetic acid only oxygen, and thus the *Mycoderma aceti* cannot and does not give to it out of its own substance The analysis of the air leaving the acetifiers shows that the oxygen required for the oxidation of the alcohol is taken from the air, and the only part that the mother-of-vinegar can take in this process is that of promoting this absorption; it is only active by virtue of this chemical process, and its place as a living plant can be taken by a large number of dead substances and parts of plants”

**Pasteur's Views on Acetification.**—The weight of Liebig's

\* *Annalen der Chem. u. Pharm.*, clvi, 137.

authority prevented the views of Kützing (*supra*) gaining much acceptance, and it was not until the year 1864 when Pasteur's experiments confirmed the conclusions of Kützing, that the vitalistic theory of acetification began to prevail, and that the acetic fermentation was recognised as being inseparably connected with the presence of living organisms

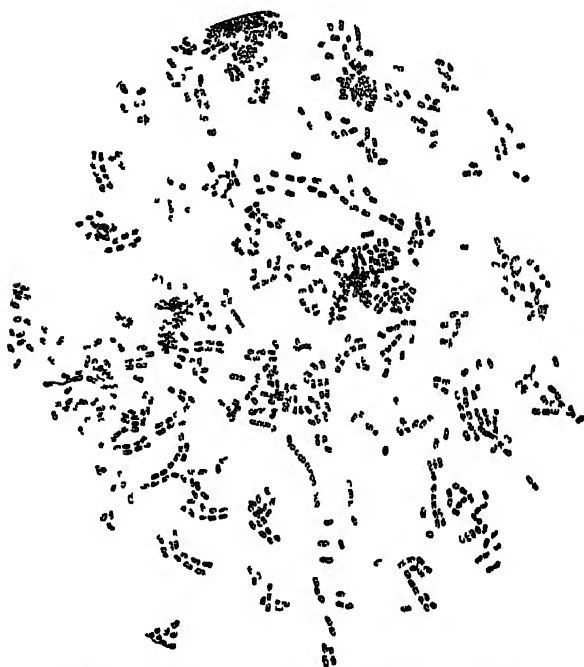


Fig 4 —Pasteur's Drawing of *Mycoderma aceti*

Pasteur observed many of the facts recorded by some of his predecessors, but he made also the first systematic study of the process of vinegar-making, and was the first to prove that no acetic fermentation could take place in the absence of the so-called fungus *Mycoderma*.

Like Kützing, he found that this mycoderma was composed of distinct cells, and in a lecture given in

1868 to the vinegar manufacturers of Orleans he illustrated the structure of the "fungus" by the drawing here reproduced

He was the first to suggest that a distinction should be made between the pellicle forming upon fermenting wine and that upon souring wine, and that the name of *Mycoderma vini* should be given to the former, and that of *Mycoderma aceti* to the latter

For very many years these names were generally accepted, but the work of Hansen and others (*infra*) showed that the organisms composing "mother-of-vinegar" were in reality bacteria, and ought, therefore, to be distinguished from the yeasts which composed the pellicle of *Mycoderma vini*. In fact, Pasteur concluded that there were many reasons for regarding *Mycoderma aceti* as a parasite of *Mycoderma vini*

In his treatise upon the Fermentation of Vinegar,\* Pasteur showed that the vinegar *Mycoderma* could be grown upon a neutral fluid containing alcohol, and that in its growth it absorbed oxygen from the air

The experimental apparatus by which he proved this fact is shown in the accompanying figure

As the pellicle developed upon the liquid in the flask the oxygen was slowly absorbed, and the mercury contained in the basin, L, gradually rose in the tube D E. Subsequently the gases remaining in the flask were withdrawn into the eudiometer F G H, while the amount of acetic acid produced was estimated by titration of the liquid.

In answer to Liebig's assertion (p. 23), that the function of the *Mycoderma* was a purely chemical one,

\* *Memoire sur la Fermentation Acetique*, Paris, 1868.

and that its place as a promoter of oxidation could be taken by dead vegetable matter, Pasteur replied that, while such a notion was conceivable, he was not concerned with this or that theory, but only with the fact that every fermentation of alcohol into acetic acid resulted in the spontaneous development of *Mycoderma aceti* in the liquid in the casks. It was, moreover, possible to keep beer yeast for many years in contact with ferment-

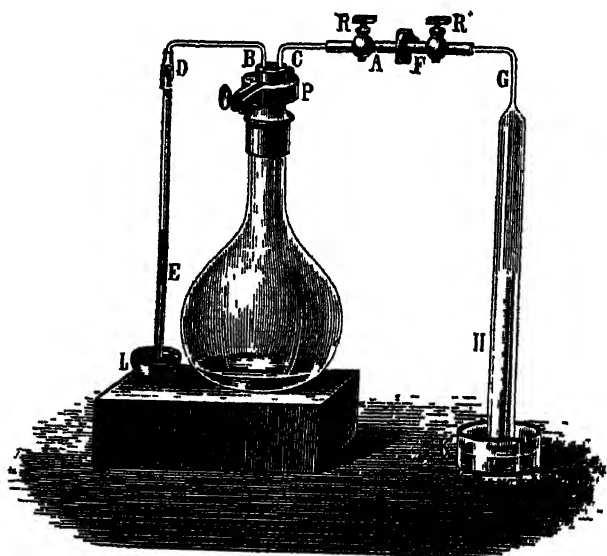


Fig 5—Pasteur's Experiment illustrating the Absorption of Oxygen

able fluids, and in communication with the air in fermentation vessels, without the slightest trace of vinegar being produced, so long as there were no indications of the appearance of *Mycoderma aceti*.

Upon the question of the presence of a specific oxidising ferment as distinct from the vital processes in the living organism, Pasteur did not express any dogmatic opinion, although from the general trend of his arguments he

appeared to have a strong leaning towards the view that both alcoholic and acetic fermentations were purely physiological processes inseparable from the life of the organisms effecting those fermentations, and he summed up his position in the matter by quoting the following words of Dumas \* —“ There are doubtless cases in which a secret agency of living organisms, such as, for example, those which are found in association with vinegar fermentation, is conceivable, but so long as the ferments in question have not been separated from the rest of the materials and the phenomenon attributed to them demonstrated, the doubt as to their actual existence must remain ”

While recognising that the vinegar “ fungus ” was not the same organism as the wine “ fungus ” or yeast, Pasteur did not agree with the view first put forward by Stack,† that the vinegar organism could be classified with the bacteria

**Nageli’s Mechanical Theory.**—In 1879 Nageli‡ put forward a mechanical theory to explain the nature of fermentation processes. According to this theory the molecular groups composing the protoplasm of an organism inducing fermentation are in a state of molecular vibration. These vibrations it is able to communicate to other compounds with which it comes into contact, so as to produce also within their molecules specific vibrations which result in the destruction of the equilibrium and the formation of new compounds.

A sharp distinction is drawn between fermentation and enzymic action, the enzymes being regarded as

\* *Chimie Appliquée aux Arts*, vi, 341 (1843)

† *Intellectual Observer*, 1863

‡ *Theorie der Gährung*, 1879

replaceable by chemical agents, whereas a ferment cannot exist apart from the living cell. It is only when work is to be done at some distance from the cell that the organism excretes an enzyme.

Applying his theory to the acetic fermentation, Nageli suggested that the protoplasm of the acetic bacteria was in a condition of molecular vibration, and that the vibrations were imparted, in the first place, to the molecules of alcohol and oxygen that had penetrated into the bacterial cells, and were thence communicated to the molecules outside the cells. As soon as the vibrations reached a certain pitch of intensity the molecular equilibrium was destroyed, chemical reaction took place, and a new series of bodies in another phase of equilibrium was produced. Part of the acetic fermentation thus occurred within the cells of the bacteria, but the greater part took place in the surrounding medium. The fermentation was thus accomplished in two stages, the equilibrium of the molecules being first destroyed, and new compounds then formed under the influence of the forces set in motion by the communicated vibrations.

**Later Enzymic Theories.**—In the later modification of his theory (p. 23), Liebig adopted a position which receives experimental support from the discovery and isolation of the enzymes in yeast, and later in the acetic bacteria by Buchner.

It has been seen that, in their earlier form at all events, Liebig's views were diametrically opposed to any such vitalistic theory as that suggested by Kützing.

According to Liebig, "mother-of-vinegar" was not a living organism, but consisted of structureless precipitated albuminous matter, which acted like platinum



black by imparting to the oxygen and alcohol its vibrations, so that these entered into combination

Liebig's final position with regard to the question of enzymes was thus practically the same as that held by Traube \* in 1858 Traube's hypothesis was that in each organism producing fermentation there was present an enzyme of definite chemical composition, which had the power of transferring oxygen from one part of a group of molecules to another These enzymes were of two kinds—viz, (1) reducing enzymes, which could transfer combined oxygen, as in alcoholic fermentation, and (2) oxidising enzymes, which were capable of conveying free oxygen to other bodies, as in the fermentation of alcohol into acetic acid Both groups of enzymes were assumed to act merely by conveying oxygen, and not by communicating their own vibrations to the fermentable substances

This theory of specific enzymes in bodies inducing fermentation was subsequently developed by Hoppe-Seyler, who concluded that the living organisms produced the ferments required for the particular fermentation, but that these ferments or enzymes were exceedingly unstable bodies, which were inseparable from the protoplasm, and became inactive when the organism died

**The Enzyme of Vinegar Bacteria.**—When Buchner † had succeeded in isolating the enzyme *zymase* from yeast, and in proving that it was possible to effect alcoholic fermentation by means of preparations entirely free from living cells, attempts were made to separate enzymes from various bacteria by similar methods of grinding

up the cells with quartz sand and kieselguhr, and subjecting the mass to hydraulic pressure.

But in every instance the liquids expressed from acetic bacteria were inert, and incapable of effecting the oxidation of alcohol. It thus appeared as though the oxidising function of the bacteria were more intimately connected with the vital processes of the organisms than in the case of the alcohol-producing enzyme in yeast, and the failure of these early experiments to separate an oxidising enzyme confirmed the views of those who held that the acetic fermentation was purely a physiological process. It was only because the oxidation was an exothermic process of a specific character that there was any evidence for still regarding the acetic fermentation as being due to a definite enzyme.

It was not until 1906 that Buchner and Gaunt\* succeeded in demonstrating, by a totally different method, that such acetic enzymes really existed. The pellicles of "mother-of-vinegar" forming upon alcoholic liquids in course of acetification were freed from water by centrifugal force, and the residual mass of bacteria was treated, while still moist, with acetone. The resulting fluid acetone preparations were stable and capable of oxidising alcohol. Any possibility of living cells was eliminated by adding a small amount of toluene. The preparations made from cultivations of bacteria grown at 10° to 22° C were more active than those grown at 28° C. In the experimental fermentations the stable acetone preparations were ground to a paste with 2 to 4 per cent. of alcohol and chalk and 4 per cent. of toluene, and the mixtures were exposed for three days to a current of

air at 28° C As a rule, not more than 0.5 to 2 per cent of acetic acid was obtained, the maximum yield being 4 per cent

The preparations also possessed the same property as the living bacteria of oxidising propyl alcohol to propionic acid From the results of these experiments there can be no reason for doubting that acetic bacteria owe their oxidising powers to the presence of one or more enzymes

It has recently been found by Wieland\* that the enzyme thus prepared from Hansen's *B. acetii* may be used instead of palladium black as a catalytic agent for the conversion of alcohol into acetic acid, and that it is capable of effecting the change in the absence of free oxygen, provided that a substance such as quinone or methylene blue is present The function of the oxygen in the methylene blue is to absorb the liberated hydrogen, and thus prevent its combining with the palladium and rendering it inactive In the light of these experiments, the enzymic process, which is usually regarded as one of oxidation, must be regarded as a dehydrogenation process In fact, Wieland considers that he is justified in regarding all oxidations as due to dehydrogenation, and that there is in reality no essential difference between processes of reduction and of oxidation.

\* *Ber d Chem Ges*, 1913, xlv, 3327

## CHAPTER III

## THE ACETIC BACTERIA.

*Mycoderma aceti*—Hansen's Three Species—Zoogloal Condition—Involution Forms—Other Acetic Bacteria—Action of Light on Acetic Bacteria—Use of Pure Cultures

*The Mycoderma aceti*—For many years after their discovery the small organisms that compose the structure of "mother-of-vinegar" were regarded as mould fungi or yeasts, the superficial resemblances between the pellicle formed upon liquids in course of acetification and that formed upon wine by the yeast then termed *Mycoderma vini* lending support to this view

The suggestion of Stack (p 27) that *Mycoderma aceti* was produced by bacteria was not accepted by Pasteur (1868), notwithstanding the fact that he states he had observed under the microscope indications of the multiplication of the cells by fission\*. One of the earliest authorities to recognise the nature of these micro-organisms was Cohn,† who in 1872 included them among the bacteria

**Hansen's Three Species.**—It was not until 1878, when Hansen ‡ published the results of his investigation into the nature of the micro-organisms that cause beer to turn

\* *Loc cit*, p 63

† Cohn, *Beitrage zur Biologie der Pflanzen*, II, 127 (1872).

‡ See *Compt Rend Lab, Carlsberg*, 1894, III, 1900, v

sour, that it became known that the acetic fermentation might be brought about by several species of bacteria

Subsequently it was discovered by Lafar\* that at least one species of budding fungi was capable of effecting the conversion of alcohol into acetic acid

The three species of acetic bacteria which were thoroughly studied by Hansen† were given the names of *Bacterium aceti*, *B. Pasteurianum*, and *B. Kutzingerianum*, and they differ from each other in their form and their behaviour when grown upon an alcoholic culture-medium such as beer

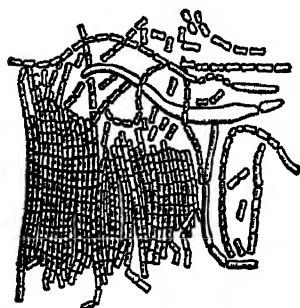


Fig 6—*Bacterium aceti*  
(after Hansen)

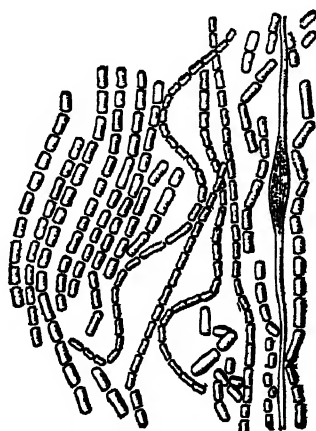


Fig 7—*Bacterium Pasteurianum*  
(after Hansen)

*Bacterium aceti*, when grown in beer exposed to the air, at a temperature of about 34° C, speedily develops a moist smooth skin, in which are markings resembling veins.

*B. Pasteurianum* also develops a pellicle within twenty-four hours, but the skin in this case is dry and has a corrugated appearance

\* *Compt Rend Lab, Carlsberg*, 1894, p 182

† *Centralbl. Bakter*, 1893, xiii, 1864

*B. Kutzingerianum* forms a skin somewhat resembling that produced by *B. aceti*, but differing from it in the way in which it spreads upwards at the edges. It also causes turbidity in the liquid, after cooling, which is not the case with the other two species

The general appearance of the cells composing the pellicles formed by these three species is shown in Fig 6

It will be noticed that the cells of *B. aceti* are smaller and narrower than those of the other two species, and that they form more compact chains than *B. Pasteurianum*. In the case of *B. Kutzingerianum* isolated cells are



Fig 8.—*Bacterium Kutzingerianum*  
(after Hansen)

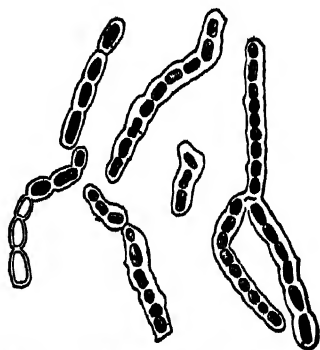


Fig 9—*Bacterium Pasteurianum*  
—Zoogloal Formation

the rule, and chain formations the exception. The constricted "figure-of-eight" forms observed by Pasteur is a frequent characteristic of the cells of *B. Pasteurianum*.

**Zoogloal Conditions.**—The curious pellicles formed by these and other acetic bacteria upon the surface of the liquid in which they develop are zoogloal forms produced by the swelling and cohesion of the walls of adjacent cells into a compact mucinous mass.

When a portion of one of these pellicles is examined under the microscope, the structure of the mucinous

layer between the cells is invisible, but when stained by Löffler's method the cells may be seen imbedded in their gelatinous envelope.

An example of this is shown in Fig 9, which represents a portion of the pellicle of *B. Pasteurianum* stained in this manner. The three lowest spaces on the left show the mucinous membrane devoid of the bacterial cells,

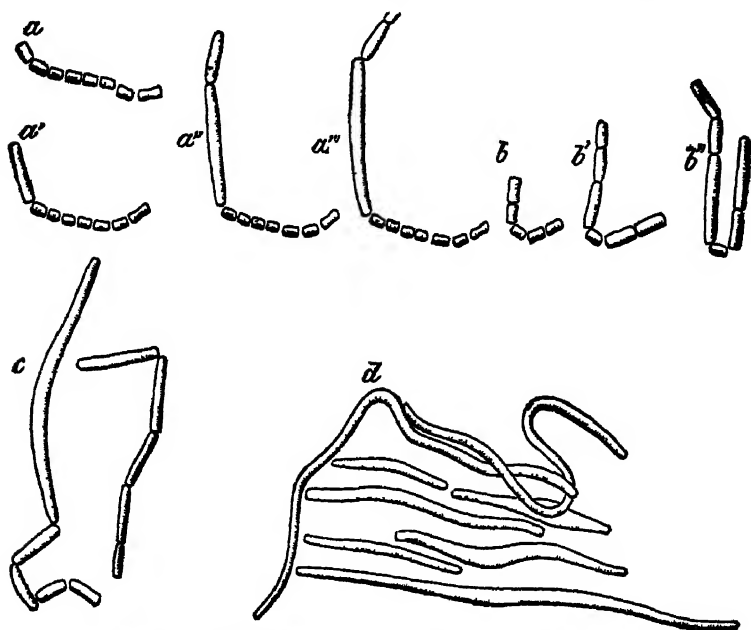


Fig 10—Morphological Changes of *B. Pasteurianum*

these having been crushed during the preparation of the specimen.

The mucinous membrane of one of Hansen's three species, *B. Kützingerianum*, when freshly grown upon a nutrient liquid, may be stained blue by a solution of iodine, and when now examined under the microscope the cells (stained yellow) will be seen enveloped in a blue medium. In the case of the other two species the cells

are stained yellow by the iodine, but the mucinous membrane remains colourless

**Involution Forms of Acetic Bacteria.**—A remarkable

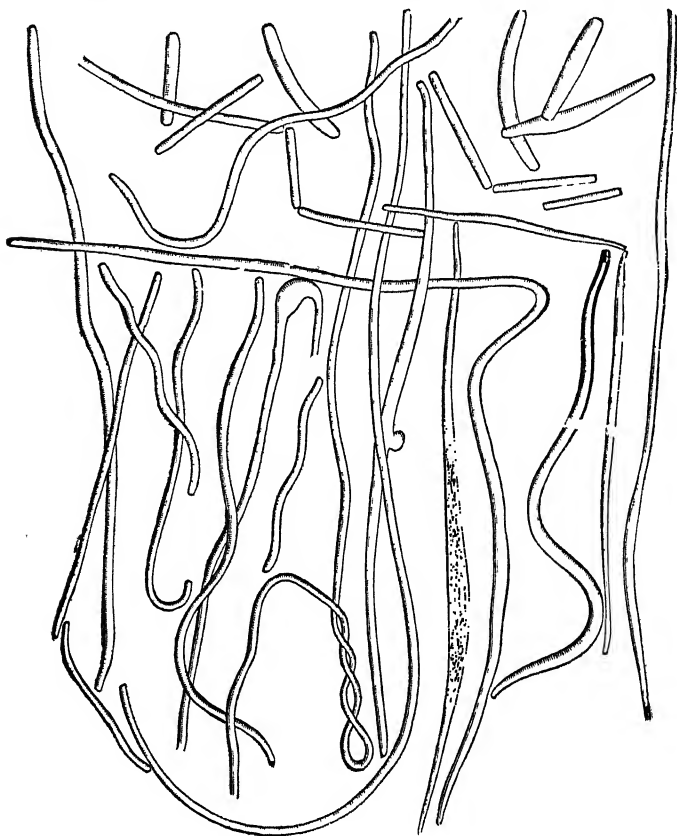


Fig 11 —Thread Formation of *B. Pasteurianum*

property, which appears to be common to all the species of acetic bacteria, is that of changing its form under the influence of temperature The discovery and investiga-



tion of this phenomenon by Hansen\* formed part of a research which has now become a classic.

Hansen found that when the cells of the bacteria,

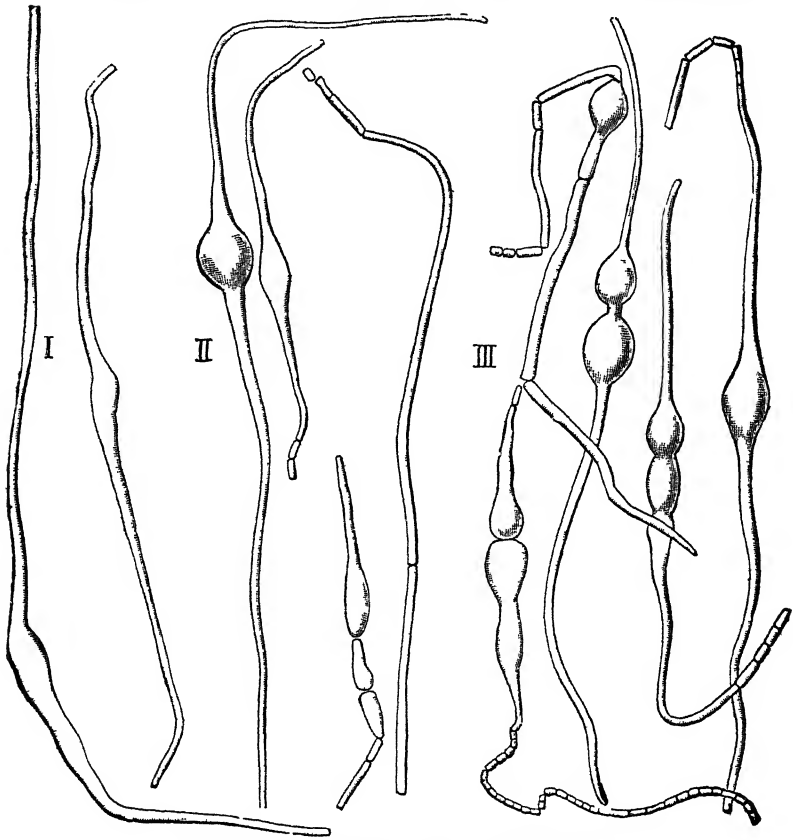


Fig. 12—Transformation of *B. Pasteurianum*

freshly grown at 34° C. (see Fig. 10), were transferred to a similar medium (a light beer), and maintained at a

\* *Loc. cit*

temperature of about  $40^{\circ}\text{C}$ , long rod-shaped forms were developed (Fig 10), and these gradually extended into long threads, some of which attained a length of  $200\ \mu$  (Fig 11)

On now exposing these filaments to the initial temperature of  $34^{\circ}\text{C}$  they began, after a few hours, to produce bulbous swellings in different places (Figs 12, 14), and finally both the rods and the bulbous cells become split up into short rods (Fig 13), leaving only the thick walls of the bulbous cell (*d*, Fig 13) unchanged

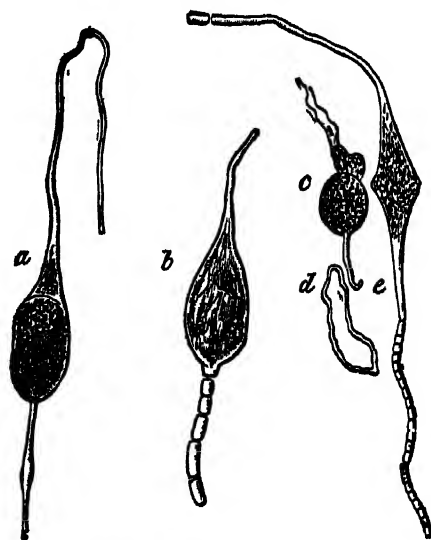
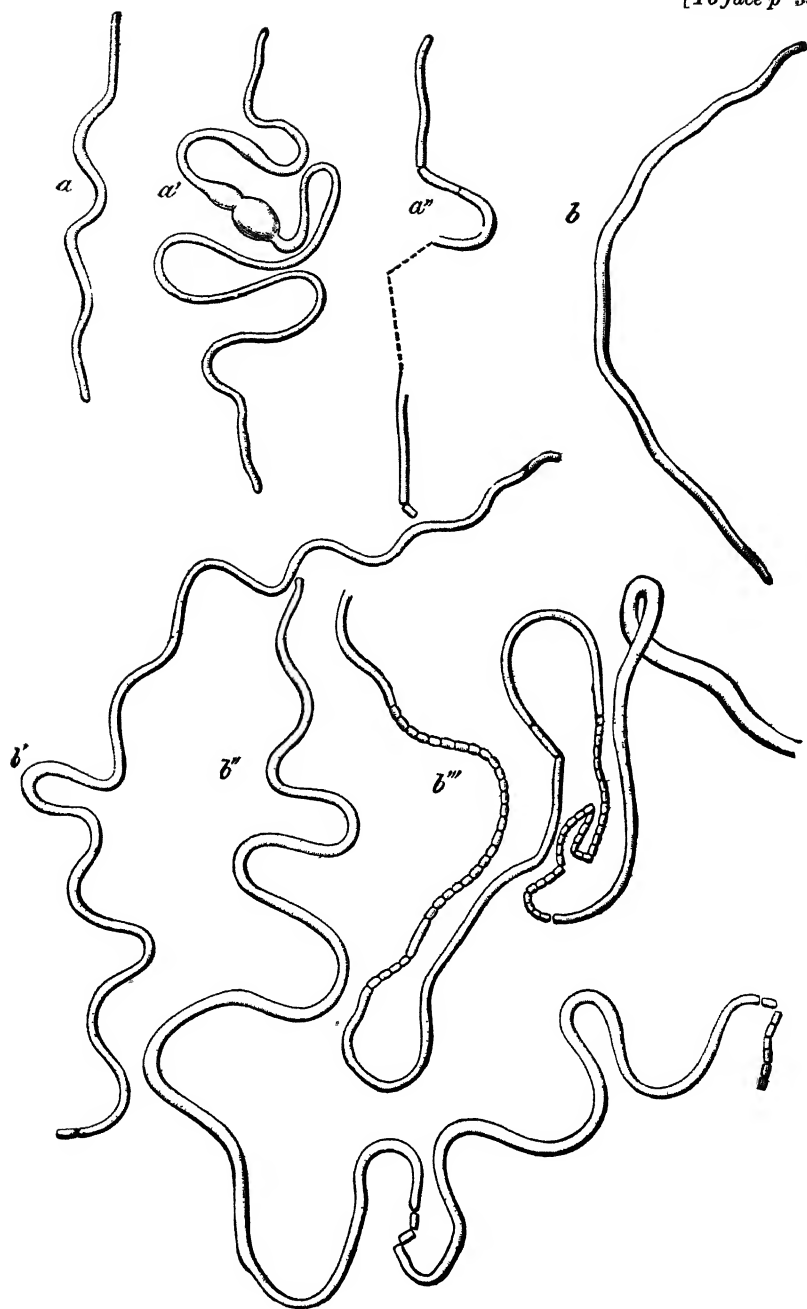


Fig 13—*B Pasteurianum*—Residue of Swollen Threads.

On examining the culture after twenty-four hours, all signs of the long thread formation had disappeared and the bacteria had reverted to their original form of chains of cells (Figs 10, 14)

These morphological changes were thus mainly dependent upon the temperature of cultivation, although they were also influenced by the composition of the





culture medium and the age of the bacteria. Cells that were more than two days old formed the long filaments with much less readiness than quite young cells.

Similar involution forms were observed in the case

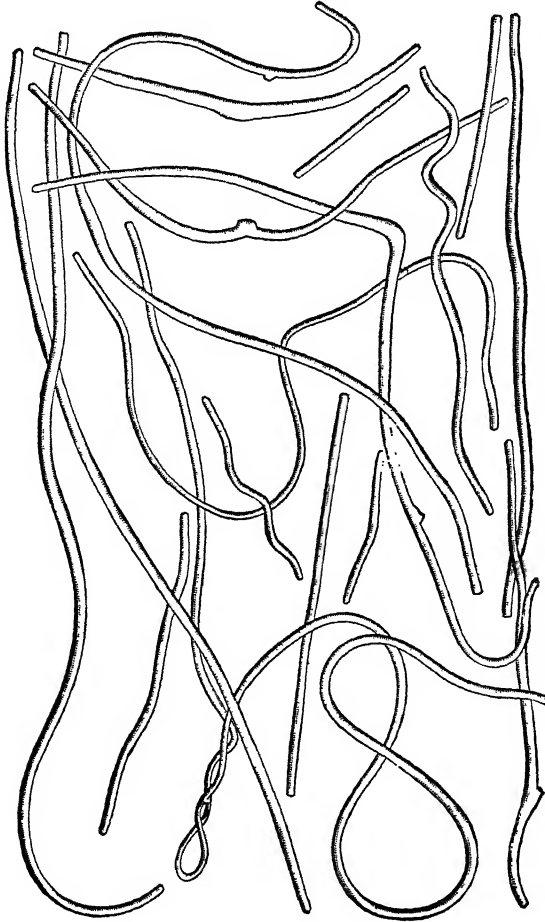


Fig. 15 —Filaments of *B. aceti*.

of the other two species discovered by Hansen. The filaments produced by *B. aceti* were thinner, and attained more than twice the length of those formed by *B. Pasteurianum* (see Fig. 15), while occasionally branchings were observed (Fig. 16)

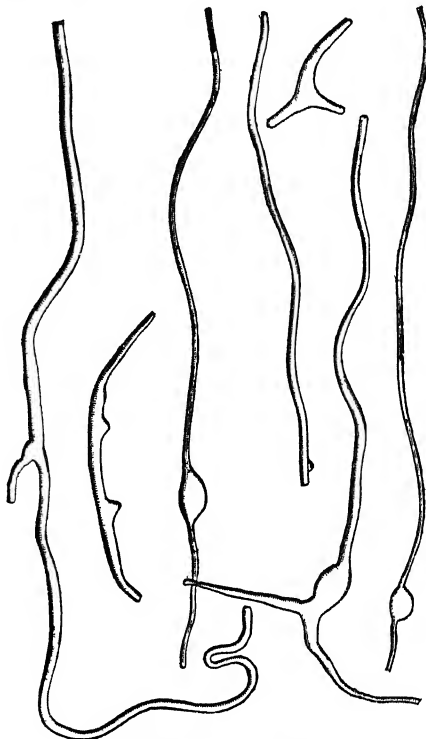


Fig. 16 — *B. aceti*—Unusual Forms.

On the other hand, the filaments of *B. Kutzingerianum*, were much shorter than those of the other two species. Hansen also recorded the occurrence of analogous formations, when other species of acetic bacteria, including

those discovered by Zeidler,\* were cultivated at higher temperatures.

**Other Acetic Bacteria.**—A species of acetic bacteria quite distinct from those described by Hansen was isolated by A J Brown † from malt wort in course of acetification, while three new species were isolated by Henneberg ‡ in 1897, and several more later §

There is some reason for doubting whether all these species are really distinct or whether some are not merely involution forms of others due to variations in the culture media

*Bacillus xylinus* (Brown)—The bacilli are non-motile rods 1 to 2  $\mu$  in length by 0.5  $\mu$  mean breadth, and under the influence of increased temperature form filaments 10 to 30  $\mu$  long by 0.5  $\mu$  in breadth. They produce a tough, gelatinous pellicle, which may grow to several inches in thickness. At first this skin is transparent, but later becomes opaque and leathery.

It is the zoogloal condition of this and allied species of bacteria which constitutes the so-called "vinegar plant," and the excessive development of which causes trouble in the working of the acetifiers in the factory.

It was shown by Brown || that when the pellicle was freed from fat, etc., by extraction there remained a mass which gave the reactions of cellulose (solubility in ammoniacal copper oxide, blue coloration with iodine and sulphuric acid) and had a composition corresponding to the formula  $(C_6H_{10}O_5)_n$

\* *Centralbl f Bakt*, 1896, II      † *Journ Chem. Soc.*, 1886, **xxxix**, 432.

‡ *Die Deutsche Essig-industrie*, 1898, II, Nos 14-15

§ *Ibid*, 1905, Nos 49-51

|| *Journ Chem Soc*, 1886, **xxx**, 432; *Proc Chem Soc.*, 1887, 87

*Bacillus oxydans* (Henneberg) —This forms rods 2.4 to 2.7  $\mu$  in length by 0.8 to 1  $\mu$  in breadth, which frequently produce long undulating filaments. It forms a thin mucinous pellicle, which does not give a blue coloration with iodine. Apparently this bacillus is identical with the *Bacterium aceti* of Zopf.

*Bacillus acetosus* (Henneberg) —The bacilli are about 1  $\mu$  long by 0.5  $\mu$  in breadth, and form long filaments resembling those of *B. Pasteurianus* in appearance. They produce a very tough, adherent pellicle, which does not give a blue coloration with iodine.

*Bacillus acetigenus* (Henneberg) —This is distinguished from the preceding species by yielding a soft mucinous pellicle, which gives a blue coloration with iodine and contains cellulose. It is one of the species which effects the acetification in German vinegar works.

*Bacillus Orleanensis* (Henneberg) —This species is stated by Henneberg to effect rapid acetification. It forms a very tough skin, which subsequently when older becomes polished and closely resembles silk paper. The bacilli form small rods (1.5 to 2.5  $\mu$  by 0.4 to 0.5  $\mu$ ), which frequently develop into long filaments. They will not grow at 8° C or at 39° C, the optimum temperature being 20° to 25° C. The pellicle does not give a blue coloration with iodine.

*Bacillus curvus* (Henneberg) —This species, in accordance with its name, has a pronounced tendency toward the formation of curved rods (1.6 to 4  $\mu$  by 0.4 to 0.5  $\mu$ ), which may occur singly or in chains. It only produces a very small quantity of pellicle, which may form small white patches on the surface of the liquid.

*Bacillus rancens* (Beijerinck) —A species of bacilli



isolated by Beijerinck\* from a beer vinegar had the property of inverting cane sugar

Several forms of bacteria were also separated by Perold† from sour wine, and termed *B. aceti vini*. He regarded them as quite distinct from other species that have been described

*Bacillus Schutzenbachii* (Henneberg) — This was found by Henneberg in the gyle of a vinegar brewery. It forms ovoid or elongated rods ( $1.6$  to  $2.4 \mu$  in length by  $0.3$  to  $0.4 \mu$  in breadth), which may be isolated or in chains. When grown on a nutrient liquid it produces pellicles which are at first in patches, but afterwards coalesce, while a light powdery deposit forms at the bottom of the vessel. The pellicle does not give a blue coloration with iodine.

*Bacillus xylinoides* (Henneberg) — Another species, isolated by Henneberg in 1906 from vinegar "wash," may produce either a thin, fairly tough pellicle, or a coarse mucinous skin resembling coagulated white of egg. The latter zooglœal condition resembles the "vinegar plant" formed by *B. xylinus*, and, like the latter, gives the cellulose reaction with iodine and sulphuric acid. The other modification of the pellicle does not give this reaction. The bacilli are rods from  $1.2$  to  $2 \mu$  in length by  $0.5$  to  $0.8 \mu$  in breadth. They will not develop at  $6^{\circ} \text{C}$ , and only grow slightly at  $15^{\circ} \text{C}$ . Their optimum temperature is  $28^{\circ} \text{C}$ , and at  $35^{\circ} \text{C}$  all growth stops.

*Bacillus vini acetati* (Henneberg) — As its name implies, this species was found in wine in course of acetification. It forms a tender pellicle, and at first causes the liquid to become turbid. The bacilli ( $1$  to  $2 \mu$  long by  $0.4 \mu$

\* *Centralbl. f. Bakt.*, 1898, **IV**, (2), 209.

† *Ibid.*, 1909, **XXIV**, 13.

broad) only occasionally form filaments Growth is feeble at 15° C and at 36° C, and stops at 8° C

**Effect of Light on Acetic Bacteria.**—Like all micro-organisms, the vitality of the acetic bacteria is reduced by sunlight, and this was recognised long before the nature of acetic fermentation was known

Thus, for example, in one of the earliest German technical treatises on the manufacture of vinegar,\* a description is given of the method of fermentation in casks, which are termed *Mutterfasser*. This process in its essential details is the same as the Orleans method described in the Transactions of the Royal Society (see p. 6), but stress is laid upon the point that all daylight should be excluded from the room, as far as possible, and that even candle-light should only be used when absolutely necessary

Experiments upon a small scale made in 1891 by Giunti † showed that acetic fermentation was inhibited by the direct rays of the sun, and that even diffused daylight checked the development of the bacteria in those parts of the liquid that it could reach These results were confirmed in 1891 by Tolomei, ‡ who also extended the experiments to ascertain which of the rays affected the fermentation. Nine samples of the same white wine were placed in a series of flasks, one of which was of ordinary colourless glass, another being blackened, while the rest were coloured in accordance with the colours of the spectrum. After the lapse of 22 days the amounts of alcohol and acetic acid were estimated in each of the flasks, with the following results —

\* Juch, *Die Kunst der Essig-Bereitung*, Nurnberg, 1818.

† Quoted by Franche, *Fabricant de Vinaigre*, p. 37.

	In Dark ness	Red	Orange	Yellow	Green	Blue	Indigo	Violet	Colour less
Alcohol, per cent by vol,	1 41	1 41	1 43	1 59	2 55	3 65	4 01	4 20	1 998
Acetic acid, per cent by weight,	5.71	5 71	5 68	5 60	4 56	3 41	3 01	2 84	4 92
Alcohol decomposed in fermenta- tion,	3 09	3 09	3 02	2 91	1 95	0 85	0 49	0 30	0 31
Acetic acid formed (+) or decom- posed (-) in fermentation,	+2 66	+2 66	+2 63	+2 55	+1 51	+0 39	+0 04	-0 21	-0 19

These results are very striking. They show a steady increase in the amount of acetic acid formed from violet to red, and prove that the violet rays of light are those that are injurious to acetic fermentation.

The precautions taken by the old vinegar makers to exclude daylight as far as possible have thus a scientific justification. When dealing with small casks, into the top of which the vinegar was poured, such constant exposure of the bacteria to the light must have had an injurious effect upon their development and action.

The experiments cited show that by placing windows of orange glass in the room the fermentation would have proceeded as well as in darkness.

When "stoves" for the large English acetifiers, containing 3,000 to 4,000 gallons, were first erected, the tradition of darkness was maintained, but the conditions of acetification on such a large scale are quite different from those that obtain in acetification in small casks.

Even when there is a top window, the amount of light that can find its way into the acetifiers through the small holes in the sides of the vats is quite negligible, and the author has proved by an experience of several years that it is possible to have sufficient light in the building without interfering in any way with the steady working of the acetifiers.

**Use of Pure Cultures of Acetic Bacteria.**—The isolation of the particular species of bacteria most suitable for the preparation of different kinds of vinegar, and their use as pure cultures for acetification, would probably give very satisfactory results in producing vinegars with different flavours, and for rapid working with different types of apparatus.

For example, the bacteria (*B. xylinus*, etc.) which form the "vinegar plant" do not work satisfactorily in some of the Continental forms of apparatus, since the heavy gelatinous slime they produce soon tends to choke any fine openings, while, on the other hand, some of the other species work best at too low a temperature to suit the large English acetifiers, which derive their heat from rapid auto-oxidation.

This is, of course, assuming that the Continental species of bacteria would not, if grown for many generations in malt wash under the conditions of the manufacture in England, gradually assume the 'slime-forming' capacity of *B. xylinus*.

So far, very little work has been done to ascertain the effects of using pure species of the bacteria in cultures prepared upon lines similar to those first employed by Hansen in growing pure cultivations of yeast from a single cell.

It was, however, shown some fifteen years ago that each individual species has the power of producing a vinegar of different quality and aroma from the same wine.

Thus Villon\* describes the results of his experiments on this point in the following words—"We have distinguished several varieties of *Mycoderma aceti*, and each of them has the property of producing a vinegar of characteristic flavour and aroma.

"We have been able to make a selection from these varieties, in exactly the same way as has been done in the case of the yeasts of beer, wine, and cider. We have

\* Quoted by Franche, *Manuel Pratique du Fabricant de Vinaigre*, 1901, p. 64.

isolated three distinct varieties, which we term I., II., and III

" *Mycoderma aceti* No. I produces an exquisite vinegar, which keeps well It acetifies wine and vinegar less rapidly than the other two varieties, and also grows old more rapidly

" *Mycoderma aceti* No II gives an ordinary vinegar of average keeping qualities It acetifies more rapidly than the variety No I, and keeps for an average length of time. It is the sort of most common occurrence in ordinary vinegar works

" *Mycoderma aceti* No III produces a turbid, flat vinegar, which keeps extremely badly It acetifies more rapidly than the others—in fact too rapidly, since it oxidises the substances that form the bouquet

"We are convinced that there are other varieties of *Mycoderma aceti*, but up to the present we have only been able to isolate these three from those which acetify wine

"It would be advantageous to make use only of *Mycoderma* No I, and to prevent the formation of No II., and especially of No III We have isolated this variety No I from Burgundy wine of an alcoholic strength of exactly 9 per cent in process of acetification at a temperature of 20° C The wine was treated with 1 gramme of ammonium phosphate per litre We then made a series of twenty cultivations in succession, the *Mycoderma aceti* not being left for longer than 24 hours in each new wine, which had previously been aerated in a current of oxygen and filtered through porous porcelain to remove foreign ferments

"We thus obtained a cultivation of *Mycoderma* which

was pure, young, and very vigorous. It was with the plant thus cultivated that we inoculated the wine that was to be acetified on an industrial scale. The ferment was only suitable for two acetifications, after which it had to be replaced by a fresh pure culture. In this way a vinegar with an excellent flavour and remarkable aroma was obtained."

It is to be feared that too little stress is laid upon the aroma of the vinegar brewed in England to make the use of pure cultures of bacteria appreciated from this point of view. On the other hand, it is possible that by the use of cultures of special species the loss of acid during acetification might be materially reduced.

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## CHAPTER IV

## CHEMICAL REACTIONS IN ACETIFICATION.

Earlier Views—Oxidation in Acetification—Effects of Oxidation—Acetaldehyde—Acetal—Ethyl Acetate—Other Products—Oxidation of the Acetic Acid—Oxidation effected by Platinum Black

**Earlier Views.**—The part played by the air in the conversion of wine into vinegar was recognised in practice long before any attempt was made to explain the facts

In the year 1778 Macquer described in his *Dictionnaire de Chimie* an experiment made by Becher, the results of which were supposed to show that wine was converted into stronger vinegar than usual when heated in a hermetically sealed flask—i.e., without the assistance of the air. Some years later the Abbé Rozier\* proved that absorption of air took place in the course of acetification. He attached a bladder distended with air to a tube passing through the bung of a cask containing wine that was turning sour, and he found that the more acid the wine became the more limp was the bladder.

**Oxidation in Acetification.**—Rozier did not draw any decisive deductions from this experiment, and it was left for Lavoisier† to show that it was not the whole of the air, but the oxygen contained in it, that was the active agent in acetification.

\* *Dictionnaire d'Agriculture*, 1786, iv., 525.

† *Traité de Chimie*, 1793, i., 159.



‘The acetic fermentation,’ he wrote, ‘is nothing more than an acidification of the wine effected in the open air by absorption of oxygen’

The nature of alcohol and acetic acid was not understood at that period, and hence Lavoisier made no suggestion as to how the absorbed oxygen acted during acetification

The theory put forward by Berthollet\* to explain the effect of the absorption in Rozier’s experiment was that the oxygen probably effected the decomposition of the vinous compound, by abstracting and combining with the hydrogen therein so as to form acetic acid, and it is interesting to note that this view has recently received support from the experiments of Wieland (p. 31) upon the behaviour of the vinegar enzyme in the absence of free oxygen

The next observations published upon the chemical process of acetification were those of de Saussure,† who claimed that he had found that during the acetic fermentation a volume of carbon dioxide equal to that of the absorbed oxygen was liberated, and that the acetification of wine depended not upon a fixation of oxygen, but upon the withdrawal of carbon and its partial liberation in the form of carbonic acid

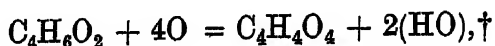
**Effects of Oxidation.**—It was not until 1821 that definite proof of the nature of the oxidation process was brought In that year E Davy ‡ discovered platinum black, and showed that when it was moistened and treated with spirits of wine it became white hot and

\* *Statique Chimique*, 1803, n. (Appendix), 525.

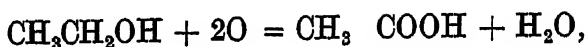
† *Recherches Chimiques sur la Végétation*, 1804, p. 143.

‡ *Schweigger’s Journ.*, 1821, i, 340.

caused the alcohol to be oxidised to acetic acid without any carbon dioxide being formed. It was this observation which suggested to Dobereiner \* his equation of the oxidation of alcohol in the acetic fermentation—



or translating this into modern formulæ—

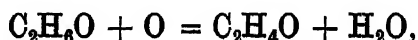


and he confirmed this by quantitative experiments.

In accordance with his results, Dobereiner explained the acetic fermentation as a simple process of oxidation, which was brought about through the agency of a body, such as platinum black, capable of condensing and absorbing the oxygen, so as to bring it into close contact with the alcohol.

**Acetaldehyde.**—Dobereiner also described a “light oxygen ether,” which he obtained by distilling alcohol with manganese dioxide and sulphuric acid. This substance, which was impure aldehyde, was subsequently studied by Liebig, who gave it its name (*Alcohol dehydrogenatus*), and showed that it was produced as an intermediate stage in the oxidation of alcohol to acetic acid.

The course of the fermentation would thus take place in two stages, in the first of which the alcohol was oxidised to aldehyde—



while on further oxidation the aldehyde became acetic acid—



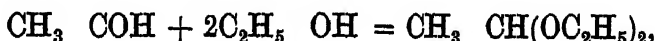
\* *Ibid*, viii, 321.

† C = 6, O = 8

This is now accepted as an approximate explanation of the main reactions that take place in the conversion of alcohol into acetic acid

The relative proportions of alcohol, acetaldehyde and acetic acid present at any given stage of the process will depend to a large extent upon the conditions of the fermentation. If too little air be supplied the secondary oxidation will not keep pace with the first oxidation, and a pronounced odour of acetaldehyde will be perceptible in the air issuing from the acetifiers

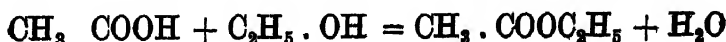
**Acetal.**—Another intermediate product formed in the oxidation is acetal,  $\text{CH}_3 \cdot \text{CH}(\text{OC}_2\text{H}_5)_2$ , which is produced when a mixture of aldehyde and alcohol is heated to a temperature of about  $100^\circ \text{C}$ —



and is also formed in small quantity through the heat of the acetic fermentation. It is probable that Doberner's "light oxygen ether" (*supra*) was a mixture of acetal and acetaldehyde, and that his "heavy oxygen ether," obtained in a later stage of the distillation, was acetal

It was shown by Kromer and Pinner\* that acetal was slowly formed by keeping alcohol and acetaldehyde together for several months at the ordinary temperature.

**Ethyl Acetate.**—In addition to acetaldehyde and acetal, a small amount of ethyl acetate or acetic ether is always produced in the acetic fermentation through the combination of the alcohol with the acetic acid—



\* *Jahresber Chem.*, 1869, 502.

In the manufacturing process this is also finally oxidised to acetic acid, so that the finished vinegar leaving the acetifiers will usually be quite free from this ester. Since, however, a trace of alcohol (about 0.5 per cent) is usually left unoxidised, slow combination takes place subsequently between this alcohol and the acetic acid, and the aroma of stored vinegar is principally due to the formation of ethyl acetate.

**Other Products.**—Traces of other alcohols, esters, and acids are also formed in the acetic fermentation, their nature and quantity depending upon the character of the non-alcoholic constituents (sugars, dextrins, acids, etc.) in the alcoholic wash. For example, formic acid is found in wine-vinegars, succinic acid in grain vinegars, and fusel oils in spirit vinegars, but although some of these compounds may influence the flavour of a vinegar, they are without practical importance in the fermentation process.

Boutroux\* gave a description of the action of the acetic fermentation upon dextrose, and showed that gluconic acid was produced. His experiments were repeated by Brown,† who found that gluconic acid was the sole product of the action of *B. aceti* on dextrose. The bacteria were unable to hydrolyse cane sugar, but oxidised mannitol, with the formation of lævulose as the main product.

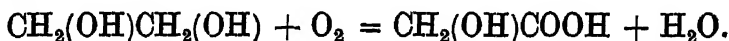
Brown's † *B. xylinus* ("the Vinegar-Plant") behaved in a similar way, but had also the property of forming cellulose from lævulose, which was not possessed by any other acetic bacteria then known (*cf.* p. 41). This

\* *Comptes Rend.*, 1880, 236.

† *Journ. Chem. Soc.*, 1886, xlix, 172.

cellulose gave all the reactions of ordinary cellulose, and on hydrolysis yielded a dextro-rotatory sugar

In this connection mention may be made of the action of acetic bacteria upon other alcohols. Both *B. aceti* and *B. xylinus* (Brown)\* are capable of oxidising propyl alcohol to propionic acid, but are unable to attack methyl or amyl alcohols. Glycerol is oxidised completely into carbon dioxide and water, with a small quantity of an unknown acid, while glycol is converted into glycollic acid—



**Oxidation of the Acetic Acid.**—It has long been known that if vinegar was left too long in the acetifiers its strength gradually decreased, but it was left for Pasteur † to prove that this loss of acetic acid was bound up with the life of the micro-organisms.

He showed that the "*Mycoderma aceti*" would develop upon a nutrient medium containing acetic acid but no alcohol, and that the air in the flask subsequently contained a large proportion of carbon dioxide but no oxygen, while the whole of the acetic acid had disappeared.

He called attention to the analogy between this slow process of combustion and the respiration of living organisms, and concluded that in the absence of alcohol the micro-organisms were capable of transferring oxygen to the acetic acid and of converting its carbon into carbonic acid.

At the same time the phenomena are also susceptible of the explanation that the oxidation of the acetic acid is due to enzymic action carried beyond the process of

\* *Ibid.*, 1887, 638

† *Loc. cit.*, p. 94.

the acetification of the alcohol, and that the carbon dioxide is not due to respiration of micro-organisms, but is a combustion process analogous to that effected by the excessive oxidation of alcohol by platinum black

**Oxidations Effected by Platinum Black.**—The analogy between the oxidations effected by platinum black and acetic bacteria furnished Liebig with one of his principal weapons against the vitalistic theory of acetification. The differences between the two processes, however, were demonstrated in 1873 by von Knierem and A. Mayer,\* who showed that the conditions were not in any way comparable, although the final products might be the same. For example, the acetic fermentation could not take place in the presence of more than 10 to 12 per cent alcohol, whereas platinum black could effect the oxidation of alcohol of any strength. In the latter case the oxidation was promoted by increasing the temperature, whereas the acetic fermentation was inhibited by temperatures exceeding about 40° C.

It was also pointed out by these chemists that the same analogies were to be observed between other fermentation processes and the hydrolytic decompositions effected by dilute acids.

For example, the conversion of starch into sugars could be effected either by diastatic "fermentation" or by the action of dilute acids. Moreover, other chemical agents, such as chromic acid, could effect the oxidation of alcohol to acetic acid.

\* *Landw. Versuchstat.*, 1873, xvi., 305

## CHAPTER V

## ACETIC ACID.

Radical Vinegar—Acetous Acid—Acetic Acid in the Pharmacopœias—Anhydrous Acetic Acid—Glacial Acetic Acid—MANUFACTURE OF ACETIC ACID—from Verdigris—from Spirit Vinegar—from the Distillation of Wood—Pyroigneous Acid—from Acetate of Lime—CHEMICAL PROCESSES OF OXIDATION—Platinum Black—Use of Ozone—Ozone in Acetifiers—Newton's Apparatus—Properties of Acetic Acid

**Radical Vinegar.**—Acetic acid, as the Latin origin of its name (*acetum*) indicates, is the acid of vinegar, from which it was first separated in a more concentrated form by fractional distillation, neutralisation with alkali, crystallisation, and redistillation of the salt with acid (see p. 3).

The strongest acid thus obtained was known as *alkalised vinegar*, or *radical vinegar*, which Bailey's English Dictionary of 1747 defines as "the sharpest Part of Vinegar, which hath its Phlegm \* drawn off"

In the London Pharmacopœias of 1721, 1746, and 1788 ordinary distilled vinegar (containing about 6 per cent of acetic acid) is described by that name (*Acetum distillatum*), but this was changed in the Pharmacopœia of 1809 to "acetic acid" (*Acidum aceticum*), and to "dilute acetic acid" (*Acidum aceticum dilutum*) in the Pharmacopœia of 1824

\* Water

**Acetous Acid.**—In the edition of 1788 the more concentrated acid is termed ‘acetous acid’ (*Acridum acetosum*)—a name which constantly recurs in Acts of Parliament down to 1844, and survives in the term “acetous fermentation,” which is still used in the vinegar industry. This name was given to the acid derived from vinegar, because it was believed to contain one atom less oxygen in its molecule than acetic acid from wood, and the salts that it formed with alkalies and heavy metals were termed *acetites*, to distinguish them from acetates. The name originated with the French chemist Berthollet, who in 1785 published a paper to prove that the acid obtained by distillation of verdigris differed in its properties from the acetous acid derived from vinegar. He regarded the acid derived from the salt as a compound of acetous acid with oxygen.

Even as late as 1806, we find the first edition of the *Encyclopædia Britannica* referring to “acetous acid in that concentrated state in which it is called radical vinegar.”

In 1808 Henry \* remarks, with reference to this question, “It appears that acetic acid differs only from the acetous in containing less water and more mucilage.”

**Acetic Acid in the Pharmacopœias.**—It was probably owing to this proof of identity that the name of “acetic acid” was given to distilled vinegar in the Pharmacopœia of 1809.

In the next edition of Phillip’s Translation (1824) it is pointed out that the “mucilage” † which passed over and condensed with the acetic acid in the distillation of

\* *Epitome of Chemistry*, 1806, p. 302.

† By the term mucilage was understood what we now describe as “extract.”



vinegar rendered it difficult to obtain pure white acetate of potash on saturating the acid with alkali. For this reason acetic acid derived from wood was introduced into the *Materia Medica* under the name of "stronger acetic acid distilled from wood" (*acidum aceticum fortius ē ligno destillatum*). At that time the strongest acid known had a specific gravity of 1.043, and contained about 32 per cent of acid, or five times as much as distilled vinegar.

In the following edition of Phillip's *Translation*, published in 1836, this "stronger acid" was described as "acetic acid" without any qualification, and was stated to contain 30.8 per cent of the anhydrous acetic acid, while *glacial* acetic acid, the strongest acid procurable, became solid at about 40° F, and consisted of one equivalent of anhydrous acetic acid and one equivalent of water. No alteration was made in the next issue in 1851.

In the first edition of the *British Pharmacopœia*, published in 1867, "acetic acid" was prescribed to contain 28 parts of 'anhydrous acid,' corresponding to 33 parts by weight of the hydrated acid. This corresponded in strength with the acetic acid of commerce and the "Purified Pyroigneous Acid" of the *Dublin Pharmacopœia*, but was not so strong as the "*Acetic Acid*" of the *London Pharmacopœia* (*supra*). It was much weaker than the "Acetic Acid" of the *Edinburgh Pharmacopœia*, which contained upwards of 95 per cent of acid.

**Anhydrous Acetic Acid.**—Considerable confusion has been caused through the belief which was at one time generally accepted, that acetic acid did not exist in the anhydrous state, and was only known in combination

with water or a base. In other words, the compound we now describe as acetic anhydride was formerly regarded as the hypothetical acid "Anhydrous acetic acid," as existing in dry sodium acetate, was assigned the formula  $C_4H_3O_3$ ,\* while glacial acetic acid was regarded as a monohydrated acid,  $C_4H_3O_3, HO$ , crystallising at  $45^\circ F$ . The hypothetical anhydrous acid was also known as *acetylic acid*, from being regarded as a compound of the radical *acetyl*,  $C_4H_3$ ,\* and oxygen. This use of the term *radical* was a development of the idea connoted by the word in *radical vinegar* which was in use long before the discovery of oxygen.

According to Nicholson,† the term *radical* was used in 1823, to describe "the distinguishing part of an acid, by its combination with the oxygen common to all acids." Thus sulphur was the radical of sulphurous and sulphuric acids.

The terms "dry" acetic acid and "real" acetic acid were used as synonyms of anhydrous acetic acid, and this must be borne in mind in calculating the strengths of acetic acid mentioned in the earlier Pharmacopœias. In the *British Pharmacopœia* of 1867 reference is made to both acetic acids, and to prevent mistake the chemical formulæ are given, showing that by "real" acid the anhydrous compound was understood.

In the *Pharmacopœia* of 1885, however, the term "real" acid is used to describe the hydrated acid,  $CH_3COOH$ , thus increasing the confusion, but in the current issue all ambiguity has been avoided by the use of the chemical name "hydrogen acetate."

\* Old notation  $C = 6, H = 1, O = 8$

† *Dictionary of Chemistry*, 1823

In 1874 the Society of Public Analysts adopted 3 per cent of "real" acetic acid as the minimum limit of strength for vinegar. It is doubtful whether this was intended to refer to the anhydrous acid (acetic anhydride) or to hydrogen acetate. Allen, speaking in 1893 on the subject,\* was not certain upon the point, but was inclined to believe that acetic anhydride was meant.

**Glacial Acetic Acid.**—The most concentrated solutions of acetic acid were first obtained by saturating dry charcoal with vinegar, and distilling the mass. Then, by exposing the later fractions of the distillate to a freezing mixture, the water separated as ice, while a stronger acid could be drained off the crystals. Only a relatively weak acid could be thus prepared, and prior to the introduction of wood acid all concentrated acids were prepared by dry distillation of verdigris or copper acetate. Acid derived in the first instance from the distillation of wood soon displaced the acid of higher strength derived from vinegar.

It is interesting to follow in the successive issues of the London Pharmacopœia how the concentrated acetic acid of commerce became purer and more concentrated. In Phillip's *Translation* of 1824 there is no mention of the glacial acid, and the author states that he has not met with acetic acid of greater strength than 30 per cent. In the next edition (1836) there is a reference to glacial acetic acid, "so-called from becoming crystalline at about 40° F.," while in the following edition (1851) the solidification point is given as 45° F. In the first edition of the *British Pharmacopœia* (1867) glacial acetic acid is included as a drug, and is stated to

\* *Analyst*, 1893, xviii, 183.

crystallise at  $34^{\circ}\text{F}$  and remain solid until the temperature reaches  $48^{\circ}\text{F}$ , while in the editions of 1885 and 1898 glacial acetic acid is required to have a specific gravity, of 1.058, and to remain crystalline above  $60^{\circ}\text{F}$  ( $15.5^{\circ}\text{C}$ )

### MANUFACTURE OF ACETIC ACID.

The earliest method of preparing a strong acetic acid from vinegar has already been mentioned (p. 57). Another process of concentration was to freeze the stronger fractions obtained in the distillation of vinegar, and to separate the crystals from the unfrozen acid.

**Acetic Acid from Verdigris.**—But the chief source of acetic acid prior to the discovery of pyroligneous or wood acid was copper acetate, which was popularly known as *distilled verdigris*, from the use of distilled vinegar in its preparation. This salt was obtained by the action of a crude vinegar, derived from refuse grapes, upon plates of copper. These were placed on wooden gratings, which were suspended in the vinegar for about three weeks, after which they were removed, exposed to the air for a day or two, and again immersed in the vinegar. In many parts of France each farm house had its *verdigris cellar*, where all wine that had become sour was thrown into tubs kept for the purpose.

As soon as the plates had become sufficiently coated with the crystals the acetate was scraped off and sold in its moist condition to the dealers.

This salt was a basic acetate with a composition approximating to the formula  $(\text{CH}_3\text{CO}_2)_2\text{Cu} \cdot \text{CuO} \cdot 6\text{H}_2\text{O}$ . When it was dissolved in distilled vinegar and the solution

crystallised, normal cupric acetate,  $(\text{CH}_3\text{CO}_2)_2\text{Cu} \cdot \text{H}_2\text{O}$ , was obtained

The crystals of copper acetate were known to the alchemists, who termed them *Crystals of Venus*, and the distilled acetic acid or *radial* or *aromatic vinegar* of the apothecaries was derived from this verdigris by dry distillation in a stoneware retort, which was gently heated in a suitable furnace (see Fig 17) The acid vapours were condensed in a series of receivers, the last of which was connected by means of a Welter's tube with a flask partly filled with distilled vinegar

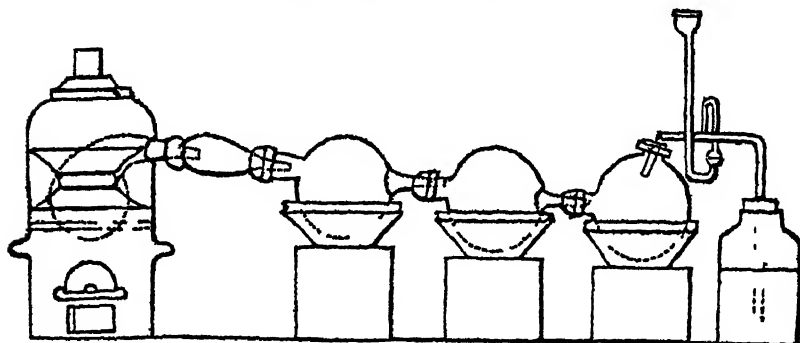


Fig 17 —Apparatus for Distillation of Radical Vinegar

When vapours were no longer distilled, and the receivers in the basins of water remained cool the process was finished. The acid thus obtained was of a green colour from the traces of copper acetate carried over mechanically in the distillation. It was purified by redistillation in a glass retort heated in a sand bath.

About a fifth of the available acetic acid was lost in this process through being decomposed by the heat. To obviate such loss the verdigris was heated with a small amount of sulphuric acid; but this had the drawback of yielding a distillate containing sulphurous acid,

while lacking the pleasant aroma (the so-called pyro-acetic spirit) of the product obtained by dry distillation. Hence, long after the introduction of wood acid, the process described above continued in use for the manufacture of "aromatic vinegar." It was not until the method of purifying wood acid had been perfected that it was finally superseded.

**Preparation from Spirit Vinegar.**—The commercial spirit vinegar (*Essig-spirit* or *Spritessig*), containing about 12 per cent of acetic acid, is used as the source of a concentrated acetic acid of about 80 per cent strength, which fetches a much higher price than acetic acid derived from wood.

Such concentration is not possible simply by fractional distillation in an ordinary retort, since the stronger fractions which pass over towards the end of the distillation are contaminated by products of the decomposition of extractive matters in the vinegar.

To obviate this, Steim devised a method of raising the boiling point of the vinegar by adding to it about one-third of its weight of salt. By this means a considerably larger yield of acetic acid was obtained, though a large proportion was still left in the retort. The distillation was carried out in tin or copper retorts.

Although a much stronger product than the original vinegar was obtained in this way, the method has been superseded by the process of neutralising the *Essig-spirit* with lime, evaporating the liquid to dryness, and distilling the crude calcium acetate with a mineral acid. The distillate has a specific gravity of about 1.060 (about 49 per cent), and is purified by further distillation with sodium or calcium acetate.

**Acetic Acid from Wood.**—The discovery that acetic acid was formed in the dry distillation of wood appears to date back no further than the middle of the eighteenth century, when Glauber described a "wood acid" or pyroligneous acid as one of the constituents of the distillate, while Boerhaave pointed out that this acid was closely related to the acid of vinegar. Glacial acetic acid was first prepared in 1793 by Lowitz, and seven years later it was proved by Fourcroy and Vauquelin that pyroligneous acid was nothing more than acetic acid contaminated with other products of the distillation. It was owing to the difficulty of completely eliminating these impurities that the identity of wood acetic acid and vinegar "acetous" acid remained unknown for so long a time.

In the year 1799 the first plant for the dry distillation of wood on a manufacturing scale was erected by Lebon, with the object of obtaining charcoal, pyroligneous acid, tar, and gas for lighting and heating purposes. A few years later a factory was started by Stoltze in Halle for obtaining pyroligneous acid from wood and converting it into pure acetic acid. About the same time the manufacture was begun in England, and in 1808 Mollerat was distilling wood at Pellerey in France, and converting the acid into a table vinegar.

An outline of his process was published in Paris,\* with reports upon the products by Berthollet, Fourcroy, and Vauquelin. It was stated that the acid there produced was of such strength that when diluted with

\* *Memoires sur la Distillation du Bois et l'Emploi de ses Produits*, par J. M. Mollerat, et Rapports faits à ce Sujet par M. M. Berthollet, Fourcroy et Vauquelin, Paris, 1808.

seven parts of water it yielded a good vinegar, and that it was identical with the acid obtained by the distillation of wine vinegar

**Pyroligneous Acid.**—The crude acid first separated from the products of the distillation is a yellowish-brown to dark brown liquid with a characteristic tarry odour. It has a specific gravity ranging from about 1.020 to 1.030, and contains not only acetic acid but also small amounts of other fatty acids (formic, butyric, valeric), together with esters, alcohols (*e g*, furfural), acetone, phenols, and tarry products. The proportions of these constituents vary with the nature of the wood, temperature of distillation, and method of condensing the fractions.

The antiseptic action of the crude acid is largely due to the presence of the phenols, and accounts for its value as an agent for curing hams and fish.

After removal of the acetone the crude pyroligneous acid is neutralised with lime, and the liquid evaporated to obtain crude brown acetate of lime. Or soda is used for the neutralisation of the liquid, which is then concentrated to obtain acetate of soda.

These impure salts are sold to the makers of acetic acid, who distil them with hydrochloric or sulphuric acid, to separate the combined acetic acid.

The acid derived from the calcium salt is known commercially as "lime acid," while that derived from sodium acetate is termed "soda acid," and fetches a higher price, owing to its usually containing less impurities, and thus having a better aroma.

**Acid from Acetate of Lime.**—The modern process of distilling acetic acid from commercial acetate of lime may



be made more clear by the following outline —On distilling together 1 ton of acetate of, say, 65 per cent. strength, and 1 ton of hydrochloric acid of 30° Tw, there will be obtained approximately—

(a) 180 gallons of strong acid of specific gravity 1 057, say, 46 per cent.,

(b) 100 gallons of feints of specific gravity 1 020, say, 10 per cent ,

corresponding together to 43 per cent acid

The strong crude acid (a), when fractionated in a column still, taking a charge of about 250 gallons, will yield approximately—

(1) 25 gallons of first runnings, used in the manufacture of white lead

(2) 150 gallons of middle fractions (specific gravity, 1 045 to 1 050) used for preparing acid (b)

(3) 50 gallons of last runnings of about 70 per cent strength

(4) 20 to 25 gallons of a residue of acid, tarry matters, fatty acids, etc

The feints (b) are neutralised with soda, evaporated, and crystallised, the crystals of sodium acetate being separated by means of a hydro-extractor, and used for the manufacture of the best “ soda acid ”

The fraction (2) is redistilled, after treatment with sulphuric acid and potassium permanganate to destroy impurities, the middle fractions being used for technical acid.

The stronger fraction (3) is also oxidised in the still, together with the similar fractions from other charges, and is redistilled to obtain higher strengths (80 per cent., to glacial acid).

In each case the first oily runnings and weaker fractions are separated, and worked up with similar fractions

### CHEMICAL PROCESSES OF OXIDATION.

**Oxidation by Means of Platinum Black.**—The process of catalytic oxidation, discovered in 1835 by Doberainer (see p 52), has been made the basis of several industrial methods, especially in Germany, where alcohol is relatively cheap

The original manufacturing apparatus of Doberainer consisted of a glass vessel in which was a series of supports at different levels. On each of these were several basins, each containing a tripod holding a watch-glass filled with platinum black. A current of air was drawn through the apparatus, while the temperature was maintained at 30° to 35° C by means of a steam coil. The vapours of the evaporated alcohol came into contact with the oxygen, and under the influence of the platinum black acetic acid was produced, and condensing upon the walls of the vessel, was collected in a receptacle at the bottom.

An apparatus with a capacity of about 700 litres, containing about 200 to 210 grammes of platinum, was capable of transforming 1 kilo of pure alcohol into acetic acid, while in some of the larger apparatus a charge of as much as 17 kilos of platinum black was employed to convert 150 litres of alcohol into acetic acid per day.

In practice it was found that the regulation of the exact quantity of air was extremely difficult. If too little was supplied a large proportion of acetaldehyde and acetal was produced, while by increasing the current of air there was a loss of acetic acid by evaporation.

A much more important drawback was that after a short time the platinum black became spent, and had to be re-calcined to render it active again—a process of necessity attended with the loss of expensive material

To obviate this a method was devised in which the platinum black was maintained at about 300° C in a porcelain tube, through which was passed a current of alcohol vapours mixed with air or oxygen

In a later modification of the process the platinum black was heated to incandescence by means of an electric current

**Use of Ozone.**—In the year 1872 a note was published by Widemann\* upon the use of ozone in the manufacture of vinegar. The process described consisted in causing the alcoholic liquid to fall drop by drop through a column containing fragments of glass or porcelain, and to meet on its way a current of hot air which had been passed through a gas flame. The action of this hot air upon the alcohol was claimed to effect acetification.

A plant to work the process upon an industrial scale was set up by Widemann in America, and numerous modifications of the process were patented.

It is open to question whether simple passage of air through a gas flame will effect ozonisation of the oxygen. Moreover, Claudon,† who repeated the experiment with air which had been ozonised in the usual way, was unable to obtain similar results. The expense of ozonisation would also be a factor against the commercial success of any such process, even if practicable.

**Ozone in Acetifiers.**—By a curious misapprehension of

\* *Comptes Rendus*, 1872.

† *Fabrication du Vinaigre* (C. Franche), p 188.

the function of ozone in any chemical oxidation of alcohol, attempts were made, especially in this country, to accelerate acetification by the introduction of ozonised air into the acetifiers

The experiments were tried on a large scale in several of the largest vinegar works in London, but in no case did they prove successful, and were abandoned after a few months' trial

It is difficult to understand the theory supposed to underlie this use of ozone, for it is a powerful bactericidal agent, and would thus be most unlikely to promote the growth or activity of acetic bacteria

The statements put forward by the promoters of some of these processes to the effect that the *Mycoderma aceti* developed more readily in the presence of ozonised air, as, for instance, when the gyle containing it was projected in a fine spray into a chamber of such air (see illustration, p 71), have not been borne out by the results of practical experience

**Newton's Apparatus.**—In the apparatus patented by Newton (Eng. Pat 1905, 1872) the use of ozone or ozonised air “produced by passing a current of atmospheric air through a flame” was claimed for effecting acetification

The liquid to be acetified was pumped from the vessel N in the form of a fine spray into the chamber A, where it meets with the ozone or ozonised air drawn or forced by means of the pump, K, from the vessel B. A series of such chambers may be superposed, the liquid leaving the bottom of each being passed in a fine spray into the next one below.

**Properties of Acetic Acid.**—Pure acetic acid is a colourless

liquid with a characteristic pungent odour of vinegar. When chilled a little below the ordinary temperature it solidifies to a crystalline mass, the solidification point depending upon the strength of the acid (*vide infra*). When applied to the skin it produces blisters, and many fatal accidents have been caused through its being inadvertently swallowed

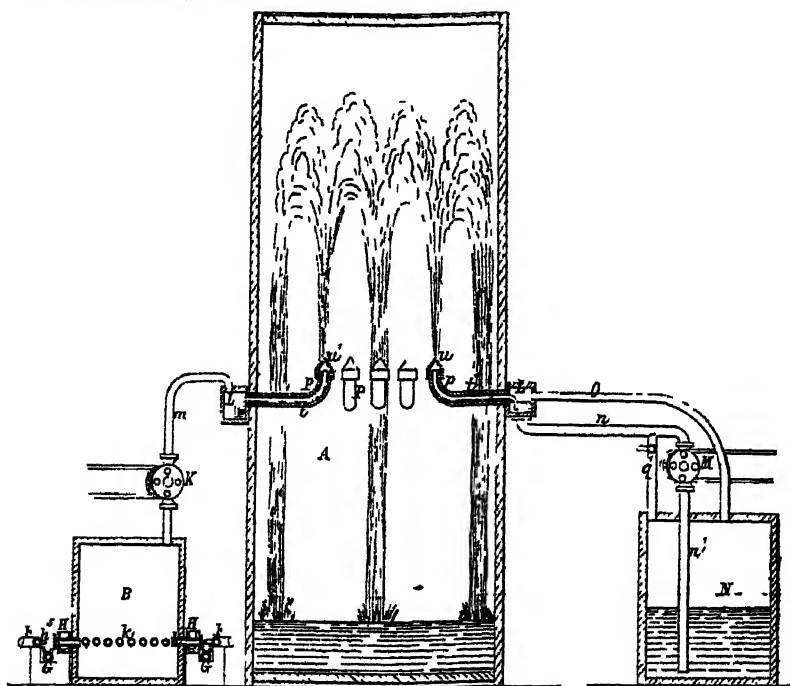


Fig 18 —Newton's Patent Process

Although an organic acid, it is remarkably stable, and is not readily attacked by oxidising agents. It can be decomposed by passing its vapour through a tube heated to redness, the products of decomposition including methane and acetone.

Most of its salts are soluble in water, several of them are of commercial importance. This aluminium acetate

and ferric acetate (*red liquor*) are used as mordants in dyeing, while verdigris (*g v*) and emerald green (cupric aceto-arsenite) form the basis of oil pigments

**Solidification Point of Acetic Acid.**—The determination of the freezing point of glacial acetic acid is one of the most reliable methods of ascertaining the amount of water present, as was first pointed out by Rudorff \* He showed that acetic acid of 100 per cent strength solidified at 16 7° C, and that with each slight increase of water the freezing point fell His results, which are given in tabular form below, did not go below mixtures containing 20 per cent of water, and his determinations were afterwards supplemented by Grimaux,† who ascertained the freezing points of mixtures of all strengths, from 93 to 16 per cent, and gave the following summary of his results —

RÜDORFF'S TABLE OF SOLIDIFICATION POINTS OF MIXTURES OF ACETIC ACID AND WATER ‡

100 Parts of Acetic Acid mixed with Water	100 Parts contain by Weight	Solidification Point	100 Parts of Acetic Acid mixed with Water	100 Parts contain by Weight	Solidification Point
		°C			°C
0 0	0 0	+16 7	8 0	7 407	6 25
0 5	0 497	15 65	9 0	8 257	5 3
1 0	0 990	14 8	10 0	9 090	4 3
1 5	1 477	14 0	11 0	9 910	3 6
2 0	1 961	13 25	12 0	10 774	2 7
3 0	2 912	11 95	15 0	13 043	-0 2
4 0	3 846	10 5	18 0	15 324	2 6
5 0	4 761	9 4	21 0	17 355	5 1
6 0	5 660	8 2	24 0	19 354	7 4
7 0	6 542	7 1			

\* *Ber d d Chem Ges*, 1870, III, 390

† *Comptes Rendus*, 1873, LXXVI., 486.

‡ *Ber. d d Chem Ges.*, 1870, III, 370.

GRIMAUD'S TABLE OF SOLIDIFICATION POINTS OF MIXTURES OF ACETIC ACID AND WATER \*

Water	Acetic Acid	Solidification Point.	Water	Acetic Acid	Solidification Point
Per cent	Per cent	°C	Per cent	Per cent	°C
7 31	92 69	+ 5 3	56 54	43 46	-16 4
13 25	86 75	- 1 4	61 68	38 2	-14 8
23 52	76 48	-11 6	69 23	30 77	-10 9
31 18	68 82	-19 3	76 23	23 77	- 8 2
33 56	66 44	-20 5	79 22	20 78	- 7 3
38 14	61 86	-24 0	81 89	18 11	- 6 4
44 50	55 50	-22 3	83 79	16 21	- 5 5
49 38	50 62	-19 8			

If these results are plotted in a curve in which the ordinates are the solidification points and the abscissæ the proportions of water, it will be found that the lines connecting the temperatures are practically straight, and that their point of intersection, showing the maximum lowering of temperature, corresponds to the mixture containing about 37 per cent of water. This probably indicates the formation of a definite hydrate,  $C_2H_4O_2 + 2H_2O$ . No break occurs at about 28 per cent of water, such as is found in the table of specific gravities at 15° C, where possibly the presence of a compound,  $C_2H_4O_2 + H_2O$ , is suggested.

It has already been pointed out (p 61) that the pharmacopœial requirements for the solidification point of glacial acetic acid have steadily been raised. In the edition of 1898 glacial acetic acid was required to contain 98.9 per cent of hydrogen acetate (by titration), and to remain solid at 15.5° C (60° F). Now, this solidification point corresponds to an acid containing not 99 per

\* *Comptes Rendus*, 1873, lxxvi., 486.

cent, but nearly 99.5 per cent, as is shown in Rudorff's table (p. 72)

In the new Pharmacopœia (1914) this error has been corrected, and glacial acid (98.9 per cent) is required not to re-melt entirely until the temperature rises above  $14.7^{\circ}\text{C}$

The point is of considerable importance in connection with the Customs duties in certain countries. For example, in New Zealand all glacial acid below the strength of that of the British Pharmacopœia is required to pay an excess duty of 5d per lb, which is considerably more than the ordinary duty.

Since the strength is ascertained, by the Customs officials, simply by determining the freezing point, acid of over 99 per cent was, prior to 1914, liable to rejection if it did not behave like acid of 99.5 per strength.

This anomaly is not found in the United States Pharmacopœia, which defines glacial acid as containing 99 per cent. of absolute acid, solidifying below  $15^{\circ}\text{C}$ , and becoming fluid again at about  $15^{\circ}\text{C}$ .

#### OPTICAL REFRACTION OF SOLUTIONS OF ACETIC ACID AT $20^{\circ}\text{C}$ (Féry)

Acetic Acid.	Refractive Index.	Acetic Acid	Refractive Index	Acetic Acid	Refractive Index
Per cent		Per cent		Per cent	
5	1.3358	40	1.3592	75	1.3755
10	1.3395	45	1.3622	80	1.3764
15	1.3431	50	1.3649	85	1.3769
20	1.3465	55	1.3674	90	1.3766
25	1.3497	60	1.3699	95	1.3749
30	1.3528	65	1.3723	100	1.3710
35	1.3560	70	1.3742		

**Optical Refraction.**—The refractive index of acetic acid shows analogous variations according to the strength.



As is seen in the foregoing table of results by Féry, it increases steadily up to about 85 per cent, where a break occurs in the curve, and the refraction falls to 1.3710 at 20° C

SPECIFIC GRAVITY OF MIXTURES OF ACETIC ACID AND  
WATER (*Oudemanns*)\*

Acetic Acid	Specific Gravity at 15° C	Acetic Acid	Specific Gravity at 15° C	Acetic Acid	Specific Gravity at 15° C
Per cent		Per cent		Per cent	
100	1 0553	66	1 0717	32	1 0436
99	1 0580	65	1 0712	31	1 0424
98	1 0604	64	1 0707	30	1 0412
97	1 0625	63	1 0702	29	1 0400
96	1 0644	62	1 0697	28	1 0388
95	1 0660	61	1 0691	27	1 0375
94	1 0674	60	1 0685	26	1 0363
93	1 0686	59	1 0679	25	1 0350
92	1 0696	58	1 0673	24	1 0337
91	1 0705	57	1 0666	23	1 0324
90	1 0713	56	1 0660	22	1 0311
89	1 0720	55	1 0653	21	1 0298
88	1 0726	54	1 0646	20	1 0284
87	1 0731	53	1 0638	19	1 0270
86	1 0736	52	1 0631	18	1 0256
85	1 0739	51	1 0623	17	1 0242
84	1 0742	50	1 0615	16	1 0228
83	1 0744	49	1 0607	15	1 0214
82	1 0746	48	1 0598	14	1 0200
81	1 0747	47	1 0589	13	1 0185
80	1 0748	46	1 0580	12	1 0171
79	1 0748	45	1 0571	11	1 0157
78	1 0748	44	1 0562	10	1 0142
77	1 0748	43	1 0552	9	1 0127
76	1 0747	42	1 0543	8	1 0113
75	1 0746	41	1 0533	7	1 0098
74	1 0744	40	1 0523	6	1 0083
73	1 0742	39	1 0513	5	1 0067
72	1 0740	38	1 0502	4	1 0052
71	1 0737	37	1 0492	3	1 0037
70	1 0733	36	1 0481	2	1 0022
69	1 0729	35	1 0470	1	1 0007
68	1 0725	34	1 0459	0	0 9992
67	1 0721	33	1 0447		

\* *Jahresber. Fortschritte der Chemie*, 1886, p. 302.

**Specific Gravity.**—Tables of the specific gravity of mixtures of acetic acid and water of different strength have been published by Mohr and by Oudemans (*supra*), but these differ considerably from each other, possibly owing to the presence of traces of higher acids as impurities in the acetic acids used for the determinations

For acids of strengths of 25 to 40 per cent a determination of the specific gravity is useful as a rough estimate of the strength, but many of the acids of 80 per strength upon the market do not comply with the specific gravity given in the tables

The tables agree more nearly for the lower strengths up to 10 per cent

BOILING POINT OF GLACIAL ACETIC ACID UNDER  
VARIOUS PRESSURES (*Landolt*)

Pressure	Boiling Point	Pressure	Boiling Point	Pressure	Boiling Point
mm	°C	mm	°C	mm	°C
1,160	132	560	109	60	48
960	126	360	96	30	31
700	119	160	73		

## CHAPTER VI.

### PREPARATION OF THE GYLE.

The Mash-Tun—Mashing Machines—Hot Liquor Backs—Process of Mashing—Gelatinised Grain—Addition of Sugar—The Conversion Process—Fermentation of the Wort—Storing the Gyle

THE first step in the manufacture of vinegar is the preparation of an alcoholic wash, containing also sufficient nutriment for the acetic bacteria

In the production of spirit vinegar in France and Germany a diluted spirit derived from potatoes or maize starch is mixed with a small proportion of phosphates and ammonium salts, and used for the purpose. Wine vinegar is made from diluted wine, and cider vinegar from sour cider or from apple juice expressed for the purpose. Any substance capable of fermentation so as to yield an alcoholic liquor is also capable of acetification under suitable conditions, but in this country the bulk of the vinegar is manufactured from malted or unmalted grain, or from a mixture of cereals and fermentable sugars

The malt or malt and grain is infused in a mash-tun or saccharified in a "converter" by means of a dilute acid, and the gyle thus obtained is clarified and acetified as subsequently described.

**The Mash-Tun.**—The most important piece of apparatus common to the brewer and the vinegar maker is the

mash-tun As the vinegar manufacture has lagged behind the brewing industry, the old-fashioned plant of fifty years ago may still be found in some vinegar works.

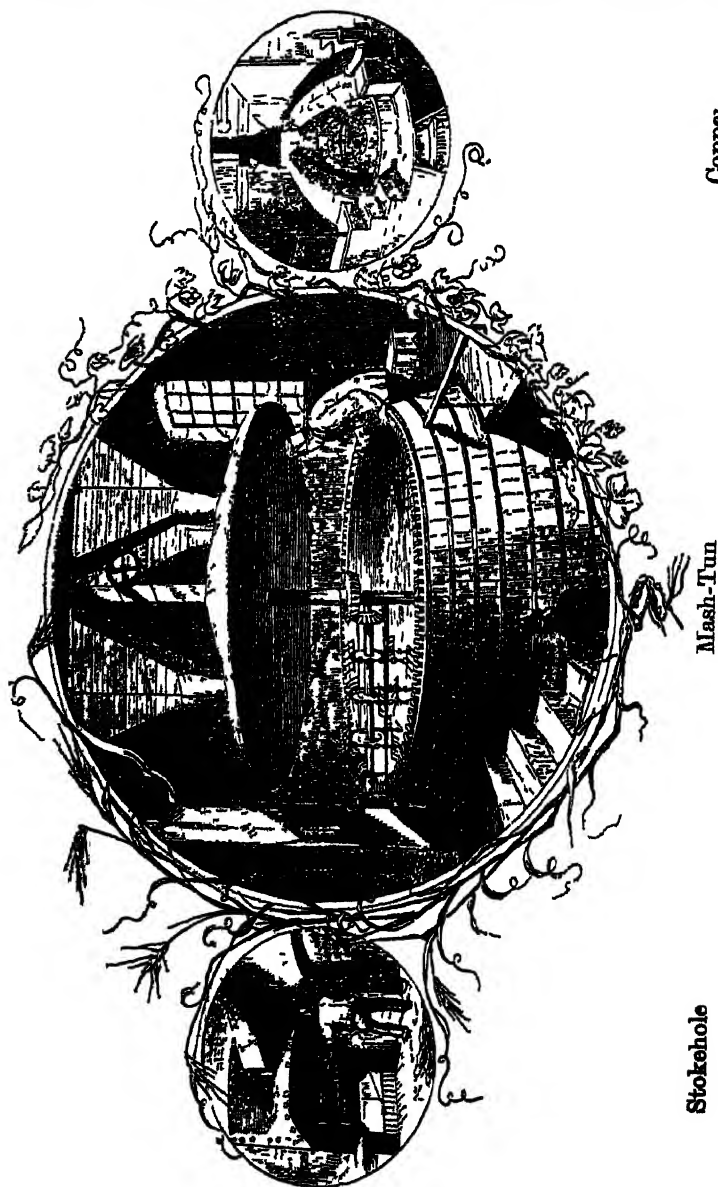


Fig 19 —Obsolete Mash-Tun and Copper

For example, an open mash-tun, like that shown in the accompanying illustration (Fig 19), in which the revolving rakes travelled round the tun by engaging in teeth upon the circumference, has been seen by the writer in old vinegar breweries

This type of mash-tun had superseded the still earlier form in which the crushed malt and hot water were

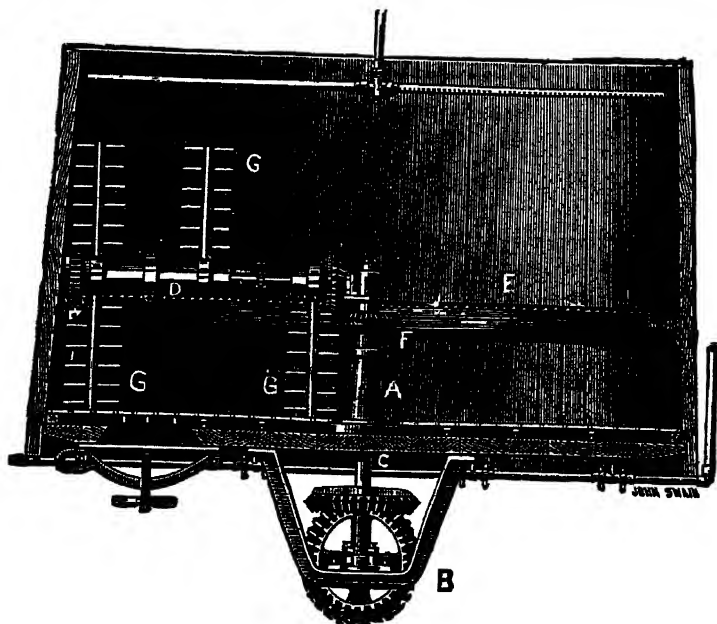


Fig 20 —Section of Mash-Tun

stirred together by long poles termed 'oars' In up-to-date vinegar works the mash-tun is completely closed in with non-conducting material, to prevent loss of heat, and it is fed by a mashing machine from a hot liquor back and grist case

The copper which supplied the older mash-tun has, in many instances, been retained for heating the water for

the first mash, but the stokehole has been abolished, and its place taken by a steam pipe

The most suitable form of mash-tun for vinegar brewing is one provided with rakes, and also with a steam coil beneath the perforated false bottom, to enable the temperature of the mash to be raised gradually from a relatively low temperature

For the reasons given below, this is much more satisfactory than raising the temperature suddenly by means of "under-letting," as is usually done in mashing malt for beer

Otherwise the construction of the mash-tun is the same as in a brewery (where it is exceptional to find mash-tuns with coils), and has the appearance in vertical section shown in Fig 20

The steam coil would be fixed in the space C beneath the perforated plates

The sparge is an essential part of the plant in a modern vinegar brewery As shown in the diagram (Fig 21), it consists of a cylindrical box or "basin," communicating at the bottom

with two arms, and is made to revolve easily about a central axis.

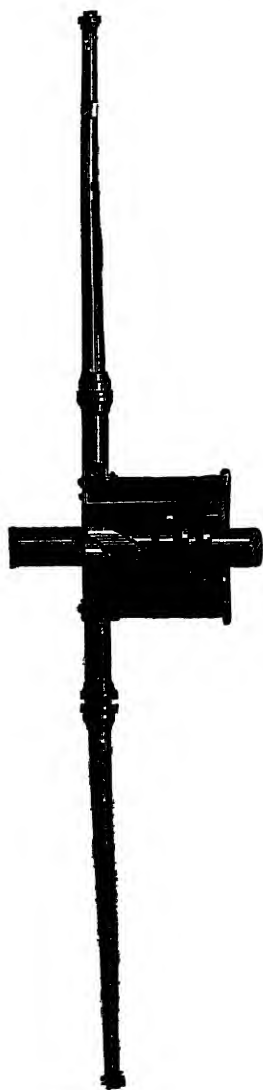


Fig 21—The Sparge

The hot water coming from the copper enters the two arms, which are perforated at regular intervals on one side, and by its pressure as it escapes from the holes causes the sparge to rotate and to sprinkle the upper surface of the mash with an evenly distributed shower.

**Mashing Machines.**—The use of an external mashing machine is particularly suitable for brewing the wort for vinegar, since it enables a more thorough and even admixture of the grain and hot liquor at any desired temperature for the initial mash to be made than is possible in the mash-tun itself

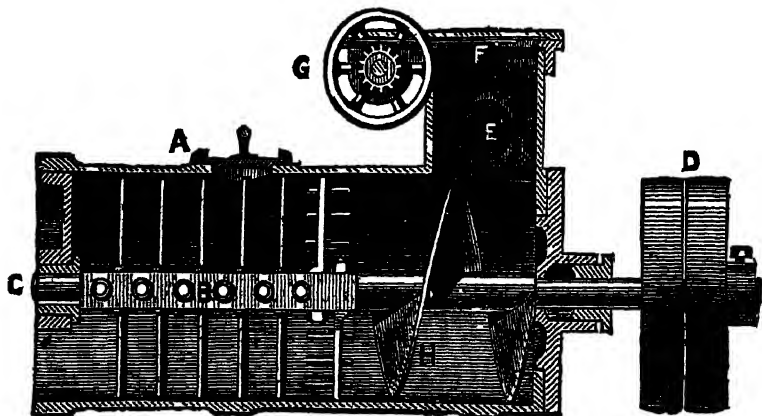


Fig 22 —Section of External Mashing Machine

The first machine of this type was invented in 1853 by Steel, and in all essentials is the same as the mashing machines still most frequently in use.

As is shown in the section (Fig. 22), it consists of a shaft B with rakes and arms at right angles, revolving in a horizontal cylinder of copper or iron A.

The screw propeller H is a modern addition, and was not present in the original machine. The shaft is made to revolve by means of a strap over the wheel D, at a

speed of 150 to 180 revolutions per minute, and thus causes a very rapid admixture of the hot water, which enters by a pipe at E with the grist which comes from the grist case through a shutter F, the movement of which is controlled by the wheel G

In another type of mashing machine the agitators are eliminated. Thus, in Matland's machine, the grist is delivered in a steady stream into a cylinder with perforated walls. This is surrounded by another cylinder, into which the hot water is forced, and is thence drawn in a series of fine jets through the perforations. At the bottom of the cylinder a larger jet of hot liquor is forced upwards, and meeting the falling grist, completes the admixture.

**Hot Liquor Backs.**—The use of coppers for heating the water for mashing has been superseded in most vinegar works by a hot liquor back, which is fixed at a level above the mash-tun, and is connected with the mashing machine, and also with the underletting pipe. This back is usually in rectangular form, and is generally made of iron cased in with non-conducting material to prevent loss of heat.

The liquid is most conveniently heated by means of a steam pipe delivering steam into the back, and if care be taken to prevent oil or impurities from the boiler gaining admission to the water, this method is quite satisfactory.

Where, however, impurities are likely to be carried over with the steam, it is preferable to heat the water by means of a copper coil. The steam entering thus parts with its heat, and is condensed, and the water escapes through a trap at the end of the coil.



The temperature of the water in the back is indicated by a special thermometer, which is bent at right angles and fixed in an opening in the side of the back. As a rule, there is also a gauge tube outside the back to show the height of the water within. Or, in some breweries, a float attached to a cord passing over pulleys serves this purpose, the amount of liquor being indicated by the position of a counterweight at the other end of the cord, in relation to a scale.

**Process of Mashing.**—The first stage in the preparation of a malt or grain vinegar is in all essentials the same as in a distillery. In each case the object is to obtain as high a proportion as practicable of sugars in a fermentable form.

In this respect the mashing process differs from that used in the brewing of beer, where, since the aim is to leave a relatively large proportion of unfermentable dextrins, a considerably higher mashing temperature is permissible.

The vinegar brewer, like the distiller, must mash his malt or malt and grain at a lower temperature, and the boiling of the wort practised by the brewer is usually unsuitable for his purpose.

If he is using a mixture of malted and unmalted grain, he will require a malt of good diastatic power, but when malted barley is being used alone a malt of low diastatic power (say about 30) will give good results.

The malt or mixture of malt and grain is crushed in exactly the same way as in a brewery, and is then passed through a Steel's mashing machine into the mash-tun, with the calculated quantity of water to give a mash at a temperature of about 120° F.

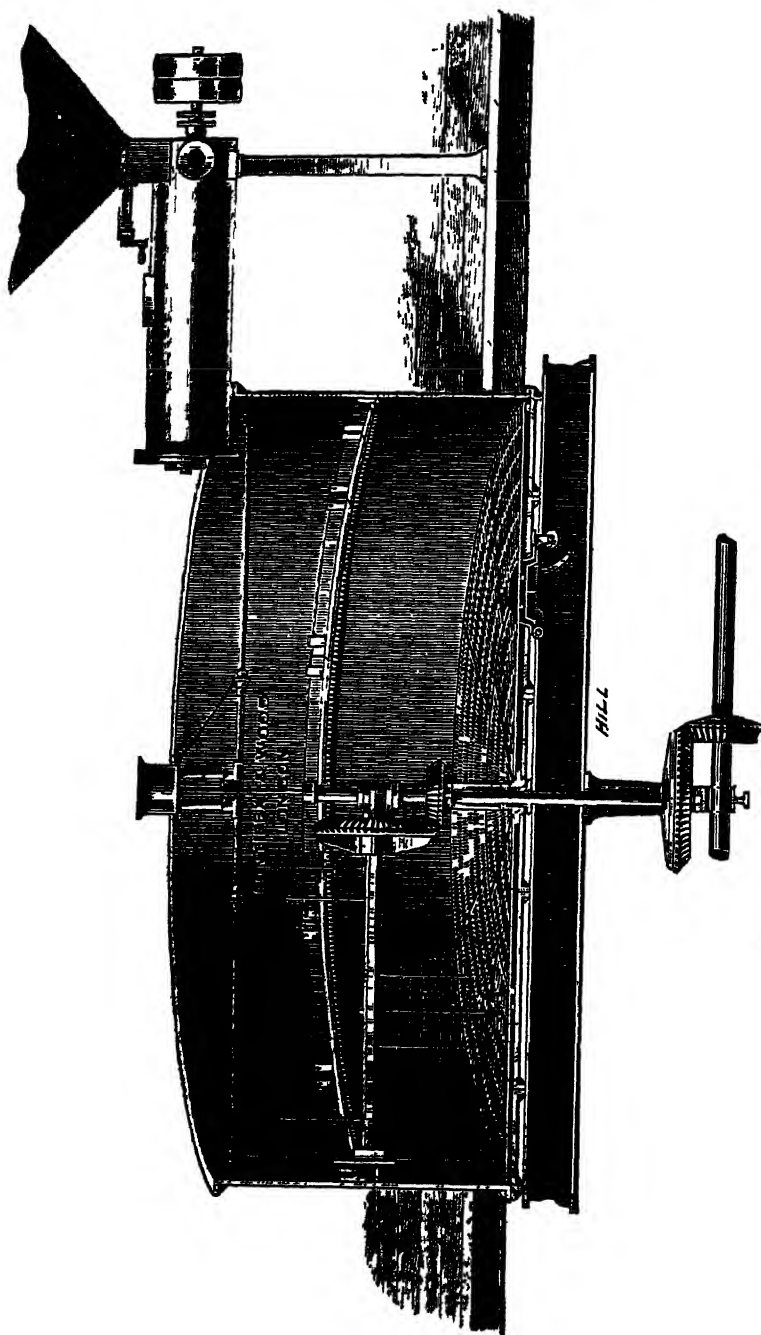


Fig 23.—Mash-Tun with Steel's Mashing Machine.

The temperature is then very slowly raised, either by underletting water at a higher temperature or, preferably, by means of a steam coil at the bottom of the mash-tun

In this connection it is of practical interest to note that in the writer's experience naked steam may be admitted at this stage into the mash-tun, without any appreciable injury to the diastase of the malt. After the temperature has in this way been gradually brought up to about 152° F., while the goods have meanwhile been kept in constant movement by the rakes in the tun, the mashing is continued until the liquid no longer gives a blue coloration with iodine

This infusion is then drained off and a second mash of an hour is given with a smaller quantity of water at 155° F., this extract being drained off as before. Finally the goods in the tun are washed from above with water at 155° F., which is distributed over their surface from the arms of a revolving sparge.

The united extracts, which will have a specific gravity of about 1.060 (from 45 quarters of malt), are cooled to about 70° F. by means of refrigerators, and are then fermented with yeast as described subsequently

A wort obtained in this way is readily fermentable, but the use of low-dried diastatic malts and low temperatures for mashing has the drawback of yielding vinegars which are sometimes very difficult to free from a slight degree of cloudiness. This turbidity appears to be partly due to albuminous substances, which can be coagulated by heat, for boiling the worts enables them to be filtered with much more ease

As a rule, however, it is not practicable for the vinegar maker to boil his worts, since by so doing he converts

dextrins into an unfermentable form, and thus reduces his yield of alcohol, and subsequently of acetic acid

In practice, therefore, it is advisable to use a malt that has been dried at a medium temperature. This will give a wort which, while fermenting well, although not giving the highest yield of alcohol, will yield a vinegar which can be made "bright" without much difficulty

A further objection to the production of an infusion containing the largest possible proportion of fermentable sugar is that the vinegar prepared from such a wort will contain very little solid matter, and that there will, therefore, be a possibility of its being condemned as an adulterated article under the Food and Drugs Act

**Gelatinised Grain.**—By submitting the grain to a preliminary heating, the starch granules swell up and become gelatinised, and are then much more readily attacked and dissolved by the diastase of malt

For this reason it is possible to use a much larger proportion of grain of this description than of ordinary untreated or "raw" grain, with the malt in the mash-tun, or to use a malt of much lower diastatic power

**Torrefied or "popped" barley** is one of these products. It is prepared by heating the barley until the starch granules are ruptured and the grain is slightly roasted. In the process of roasting the moisture of the barley is reduced to about 3 to 4 per cent, while the fat is lowered by about 50 per cent, both of which changes are advantageous from the brewing point of view

**Flaked Maize and Rice.**—As the large amount of oil in the maize is of no use to the brewer, preparations known as "flaked maize" or "flaked maize malt" are sold in large quantities.

They are prepared by crushing the maize, removing the germ containing the bulk of the oil, and gelatinising the starch by heat. To some extent the heating does the work of diastase, and for this reason such products have become known as "malts" in the brewing industry.

Flaked rice is prepared in a similar manner, but in that case the process is not so advantageous to good mashing, since rice contains much less oil than maize.

Analyses of gelatinised grains are given in Chap. X, and show the influence of the processes upon the composition of the cereals.

In some vinegar breweries rice or maize grits are partially gelatinised on the spot by subjecting them to the action of steam under pressure. This ruptures the starch granules, converting the whole mass into a paste, which, when cooled to about 130° to 140° F, is rapidly liquefied on the addition of a small amount of crushed malt. It can then be run into the mash-tun, where the saccharification of the starch is completed at the same time as the rest of the mash. In this way a large quantity of raw grain can be introduced into the mash-tun, without any risk of finding unconverted starch in the wort.

This entails the use of a separate vessel or "converter" for the gelatinisation of the starch of the raw grain, but by suitable manipulation and saccharification in stages it is possible to use the mash-tun itself for the purpose.

For example, a mixture of the crushed barley and malt is slowly heated from about 130° to about 170° F. The sugar formed in the hydrolysis at the lower temperatures protects the diastase for some time at the higher temperature, so that a considerable amount of the starch in the raw grain is converted. The temperature is then

raised to over 200° F, and kept at that point for about 30 minutes to gelatinise the starch, after which the mash is cooled to 130° to 135° C by means of a coil, and a fresh portion of ground malt added to complete the hydrolysis of the gelatinised starch. When now the temperature is gradually raised to 155° F, the conversion is rapidly completed, and the wort is then drawn off, and the "goods" sparged in the usual way.

**Addition of Sugar.**—Certain makers of vinegars prefer to buy the products of the acid hydrolysis of cereal starch in the form of ready-made glucose, which is sold either in the form of a thick syrup or as a solid.

A suitable proportion of the sugar is added to the wort as it leaves the mash-tun, and a much more concentrated wash can thus be prepared without the necessity of using larger plant.

Worts to which commercial glucose has been added usually "attenuate" very far, and hence in some cases yield a vinegar deficient in "body." To prevent the product being too thin in this respect special preparations containing unfermentable dextrins are sometimes used, or a certain proportion of molasses may be mixed with the glucose.

In several of the larger vinegar breweries a "converter" is used for transforming the starch of the cereal into fermentable sugar, and thus, while obtaining all the advantages of a product prepared by acid hydrolysis, they also retain the other constituents of the grain (the nitrogenous compounds and phosphoric acid), which are not present in commercial glucose.

**The Conversion Process.**—Instead of the starch of cereals being saccharified by the diastase of malt, a process

in which a dilute mineral acid is used as the hydrolytic agent is employed

Maize or rice are the chief materials used by those who prepare their worts in this way, and when malt is also added, as is sometimes the case, the object of the addition is to give a malt flavour to the product or to make it answer more closely to the normal composition of a barley malt vinegar

In converting the starch into fermentable dextrose, the grain is mixed with dilute sulphuric acid (about 3 per cent strength) in a closed iron vessel, where it is heated for several hours by steam under pressure until a sample of the liquid no longer gives a reaction for unconverted starch

The contents of the converter, which now consist largely of an acid solution of dextrose, are neutralised with lime and chalk, which precipitate the sulphuric acid as gypsum, and are then drawn off, cooled, and fermented in the same way as the wort obtained by mashing

A converter of average size will take a charge of 6 to 7 tons of grain, and the whole of the starch will be hydrolysed within about three hours, when heated with steam under a pressure of about 10 lbs. After neutralisation the mixture is allowed to stand for several hours for the calcium sulphate to subside, and is then drawn off through filters, cooled, and passed into the fermenting tuns

As it leaves the filters the wort (from the above-mentioned quantity of grain) will show a specific gravity of about 1.070, and, if a strong vinegar is required, is pitched with yeast directly without any dilution. It is more usual, however, for the liquid to be diluted with water

to a specific gravity of 1 055 to 1 060 before fermentation

Although the bulk of the calcium sulphate separates in insoluble form during the neutralisation, a considerable proportion will still remain in solution, and will afford an indication, though not an infallible one, that the vinegar has been prepared by a conversion process

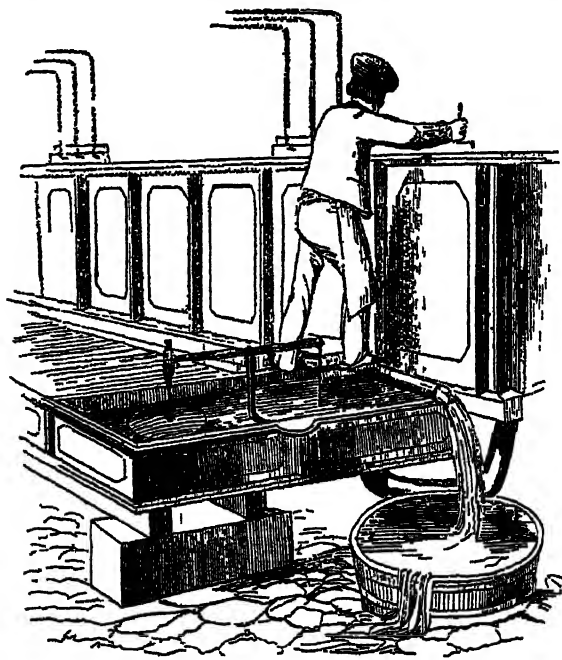


Fig. 24.—Underback and Refrigerator (A D 1812)

Usually the glucose solution derived from the acid hydrolysis of grain is readily fermentable, and a wort of specific gravity 1 060 can be attenuated without difficulty down to a specific gravity of 1 004 to 1 005. Vinegars prepared from the products of the “converter” are frequently sold as “malt vinegar,” although they do not comply with the definition suggested by the



Local Government Board, which requires the starch to have been saccharified by the diastase of malt

**Fermentation of the Wort.**—After leaving the mash-tun the wort, including the spargings, is pumped through a refrigerator to cool it down sufficiently for the addition of the yeast

In the older vinegar breweries cooling was effected by exposing the liquid to the air in large shallow tanks, known as coolers, such as that shown in Fig 24, which represents the obsolete plant used in 1812 in Messrs. Beaufoy & Co's Works But at the present day the same course is followed as in breweries, and the wort is cooled by means of refrigerators, which are usually of the vertical type

As is shown in Fig 25, the refrigerator consists essentially of a series of superposed tubes, through which passes a current of cold water The wort is pumped into a trough above these and trickles through holes in the bottom of this in a number of thin streams over the tubes, in succession, until it reaches the large trough in which the apparatus stands

The cooling tubes are frequently of oval instead of circular form, so as to offer a larger cooling surface to the liquid trickling over them

Horizontal refrigerators (Fig. 27) are sometimes employed where there is insufficient height for the other type, and when the supply of water is plentiful They are made in the form of a rectangular trough with partitions at intervals In each compartment is a horizontal tube with rounded ends, through which passes the cold water. The hot wort passes successively through these compartments, and is thus cooled in

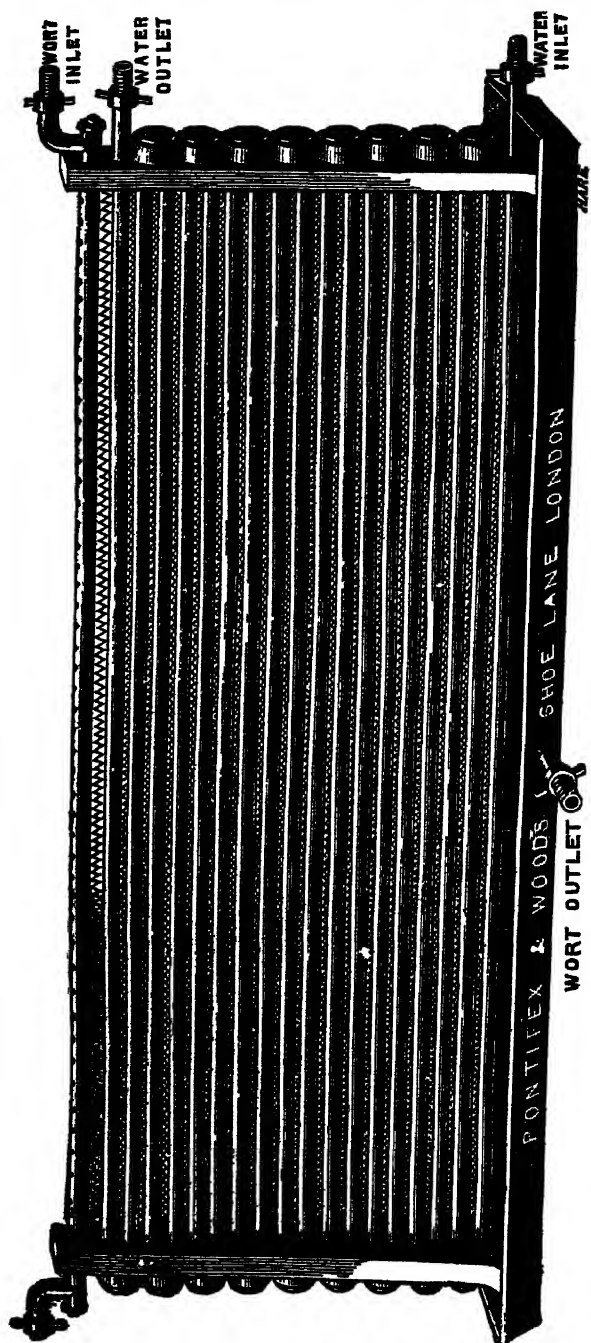


Fig 25 —Vertical Refrigerator.



Fig 26 — Exterior of Fermenting Tuns

stages before running into the main leading to the fermenting tun

Except in cases where a good growth of yeast is the primary object, it is unnecessary to cool the wort for vinegar to so low a temperature as is required for beer.

Yeast may be added to the wort at a temperature of  $70^{\circ}$  to  $75^{\circ}$  F, and although a 'boiling fermentation' usually follows, the attenuation takes place more rapidly and completely than when lower temperatures are maintained. The temperature rapidly rises, and on the second

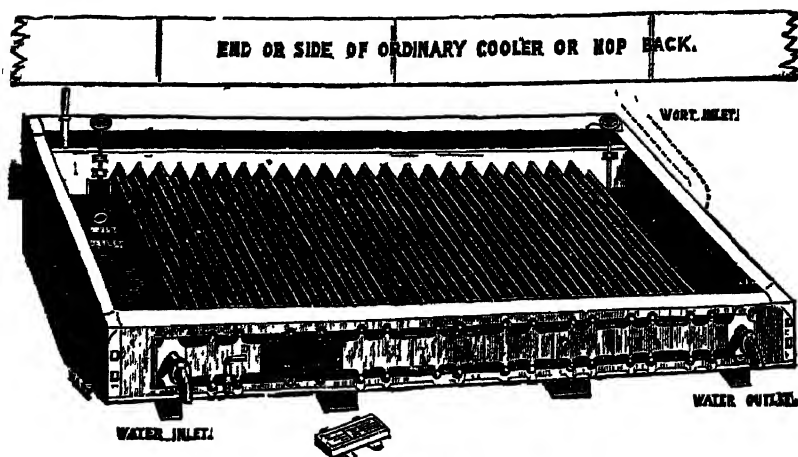


Fig 27—Horizontal Refrigerator

day will be as high as  $90^{\circ}$  to  $93^{\circ}$  F, falling on the third day to about  $85^{\circ}$  F., while the yeast working under such conditions produces very little "head"

In some vinegar factories the production of yeast is the main end in view, while vinegar is only manufactured as a by-product. In such cases the conditions to be followed are quite different from those described above. The wort must be cooled to a much lower point (say about  $60^{\circ}$  F), and, after "pitching," the temperature

in the fermenting tun must be kept at about  $70^{\circ}$  to  $75^{\circ}$  F by means of an attemperator, or cooling coil within the vat (see Fig 28).

Much more efficient aeration is also required to obtain

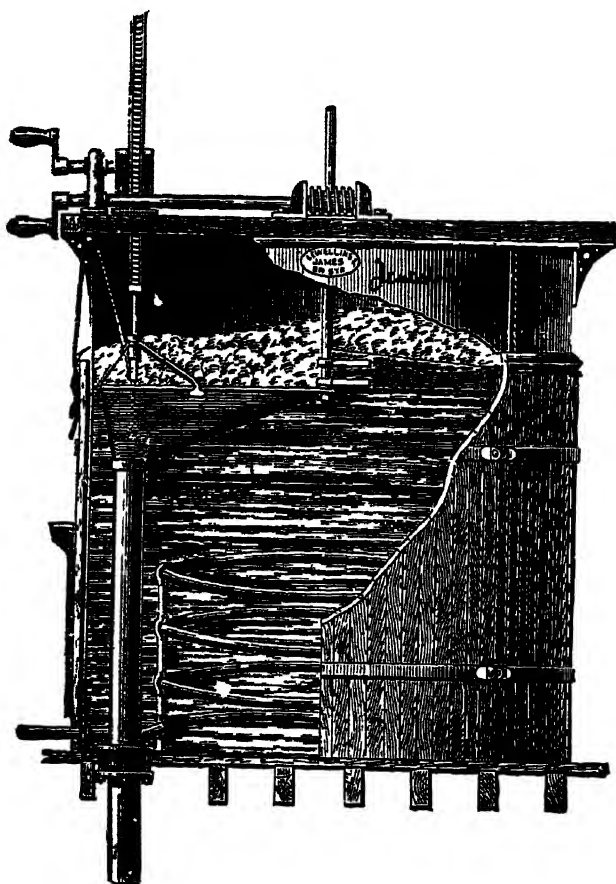


Fig 28 —Fermenting Tun with Cooling Coil and Parachute

a good crop of yeast than when attenuation of the wort is the main object. Various devices are in use for this purpose. In addition to the primitive wooden rouser, a current of air is sometimes pumped into the vat through

a tube which passes nearly to the bottom of the liquid, and terminates in a rose or perforated radial arms.

A common form of apparatus for removing the yeast from the surface of the liquid is that known as the "parachute" (Fig 28). This consists of a funnel ending in a tube, with a valve near the top, which can be controlled from the outside. The yeast is driven into the parachute by means of a metal "skimming board," as shown, and is collected in a tank below the tun, where it is washed with water, and then pumped into a press.

The parachute and skimming board are attached to a rack and pinion work, so that they can be raised or lowered at will, and means are also provided for making the skimming board sweep over the surface of the liquid.

Unless special precautions are taken to keep a low temperature and to aerate the liquid thoroughly during the fermentation, it is of little use attempting to press the yeast, since it assumes such a slimy condition that it speedily clogs the cloths of the filter press.

The choice of a yeast for the fermentation will largely depend upon which of the two modes of fermentation is to be followed. As brewing in the vinegar industry takes place more or less intermittently (with the exception of the factories that manufacture pressed yeast), it is usually not practicable to use the strain grown in the vinegar works.

Apart from that, the yeast is weakened in the high temperature fermentation, and is less suited for a following fermentation than a yeast grown at a lower temperature.

The best course to follow is to select the type of brewers' or distillers' yeast which is found by trial to be the most

suitable for the wort at the desired temperature, and to obtain a fresh supply thereof for each brewing

**Storage of the Gyle.**—After fermentation is complete

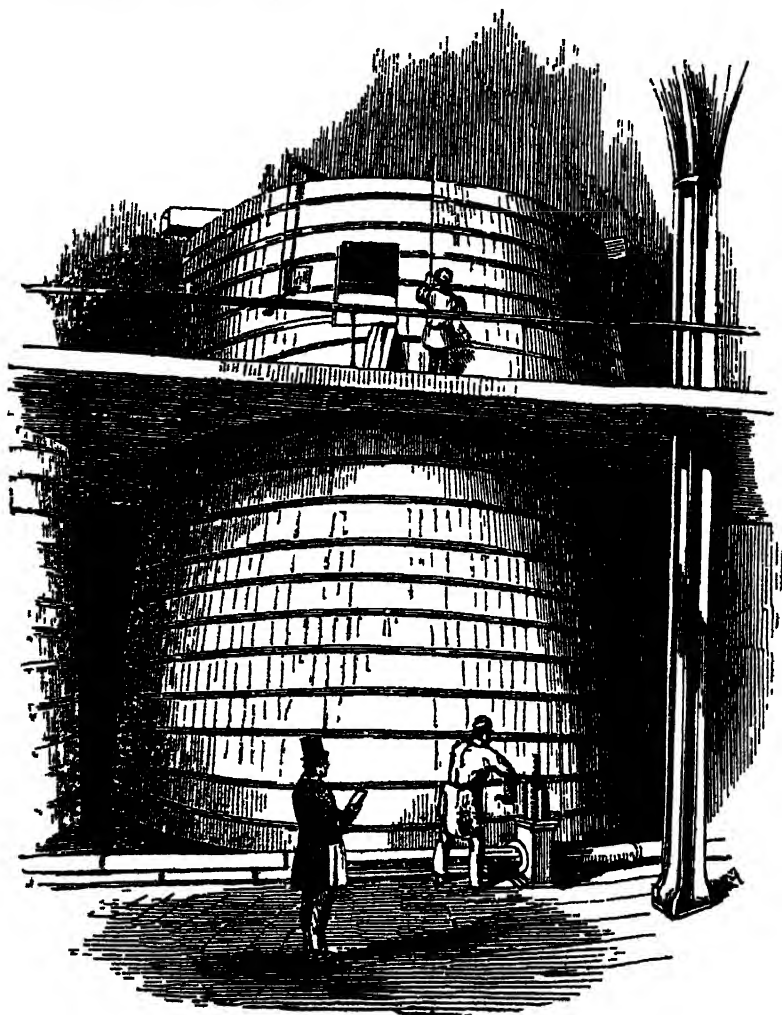


Fig 29 —Old Store Vats

the alcoholic wash is racked into storage vats, where it is left for some weeks or months before being transferred to the acetifiers. The longer this period of storage

can be made the better the wash is suited for acetification. Not only does it clarify itself spontaneously, throwing down a deposit of dead yeast cells, but it also undergoes a preliminary acetification. Hence a wash that has been stored for three months may contain as much as 2 per cent of acetic acid, and thus reduce the time required for the work of the acetifiers. It has also the advantage of keeping the acetifiers cleaner than in the case of freshly-fermented gyle, while the vinegar it produces can be obtained in "bright" condition much more rapidly than is otherwise possible.

For these reasons it is the practice in some vinegar works to do the main portion of the brewing at one time of the year, and to acetify the wash at another. It may almost be accepted as an axiom that the greater the storage capacity of the works the better the condition both of the gyle and of the finished vinegar.

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## CHAPTER VII

## ACETIFICATION OF THE GYLE.

**APPARATUS** The Slow Process—Fielding—The Orleans Process—Claudon's Apparatus—The Quick Process—English Acetifiers **DISTRIBUTION OF THE GYLE** The Sparger—The Tipping Trough—Siphon Distributors—Aeration Devices—Wagenmann's Graduator—Luck's Acetifier—Singer's Apparatus—Bersch's Acetifier **ACETIFICATION IN PRACTICE** Aeration—The Temperature—Effects of Alcohol and Acetic Acid—The Group System—Disturbances due to Mother-of-Vinegar—The Vinegar Eel—The Vinegar Mite—The Vinegar Fly

**The "Slow" Process.**—However the alcoholic wash or gyle has been prepared, it has to be subjected to the combined action of the acetic bacteria and atmospheric oxygen to convert it into vinegar. The oldest process of effecting this change was by exposing the casks partially filled to the air, with their bungs drawn out.

This method, which is now obsolete in this country, was known as "*felding*," from the fact of the casks being exposed in series of rows in the *vinegar field*.

Between each series of rows was an underground pipe communicating with a "back" at the top of the brew-house, and each cask was filled by means of a hose attached to a cock upon the distributing pipe, the top of the hose being passed from cask to cask as shown in the illustration.

During fine weather the bung-holes were loosely covered

with pieces of slate, to prevent access of dust, but during wet weather the bungs were replaced.

Several months were required for the conversion of the gyle into vinegar, the length of time depending upon the temperature of the atmosphere, and the amount of aeration that was possible by way of the bung-holes

When the fielding was finished the vinegar was drawn off by means of siphon tubes into a trough, the lower end



Fig 30 —Vinegar Field. Filling the Casks

of which delivered into a travelling tank, which could be moved up and down between the rows (see Fig 31) Thence it ran through a hose and underground into a well in the building, to be pumped into the store vats prior to filtration

This "slow" process of acetification was practically the same as the "Orleans process" of making wine vinegar, the only difference being that in the latter the

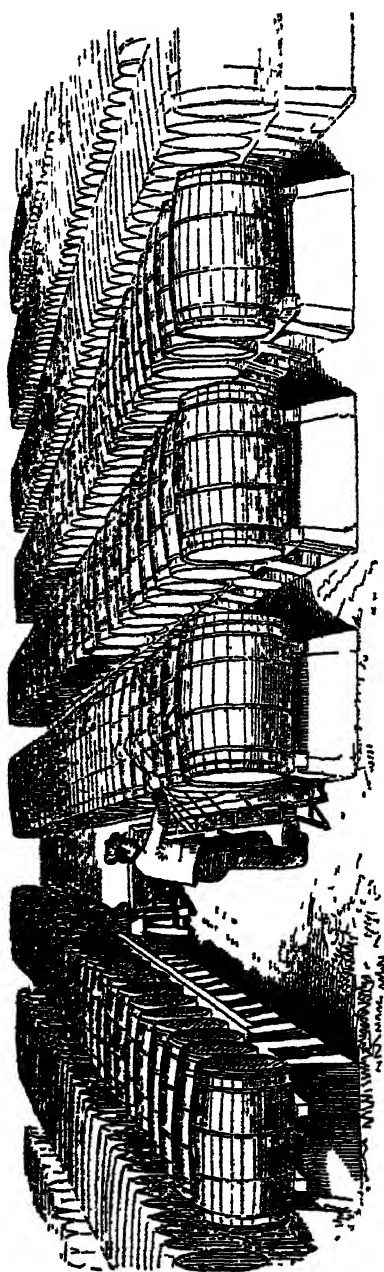


Fig 31.—Vinegar Field, Drawing-off

casks are kept in a heated building and means are provided for the admission of more air

#### The Orleans Process.

—The method of acetifying wine that has been used from time immemorial in France, and especially in the district of Orleans, whence it takes its name, is not the same as that described by a correspondent of the Royal Society in 1670 (p 5), which is essentially the modern "quick" process

According to Franche,\* the reason why the Orleans process has not been displaced by the more modern "rapid process" is that it will not acetify alcoholic solutions containing less than 25 per cent of

\* *Manuel Pratique du Fabricant de Vinaigre*, p 53.

wine Below that strength it is necessary to add phosphates and nitrogenous substances, and since these products from wine diluted with alcohol have to be sold under the name of "spirit vinegar," the Orleans process has come to be regarded as the only possible method of making pure wine vinegar

The apparatus working by the "quick method" is stated by Franche not to give satisfactory results with wine or mixtures of wine and alcohol, owing to the tartar deposited from the wine clogging the pores of the shavings or other porous material

Originally wine vinegar was made by the simple method of mixing wine with a little vinegar and exposing the mixture to the air in open casks This primitive method was in use in some small factories, even in Orleans, as late as 1876, although most vinegar makers had long discarded it in favour of the "Orleans process," in which the acetification is effected in a series of casks of special construction provided with holes for the admission and outlet of air

These casks, which are termed "mothers," are ranged in tiers, as shown in the accompanying diagram, usually in an underground cellar, the temperature of which can be maintained at a fairly constant point, while the supply of air entering through the door-way can be regulated as required The cellar is heated by means of a stove or hot-water pipes to a temperature which is never allowed to exceed 30° C (86° F.)

Prior to entering the acetifying casks the wine is filtered through a large vat containing shavings, which is known as a "wine-rape," while after acetification the vinegar is passed through a second rape, and matured in storage casks.

The average quantity of vinegar produced by each cask in a month is only about 40 litres ( $8\frac{3}{4}$  gallons), and the expenses of manufacture range from about 3 to  $3\frac{1}{2}$  francs per hectolitre

The drawbacks of the Orleans process are that it is

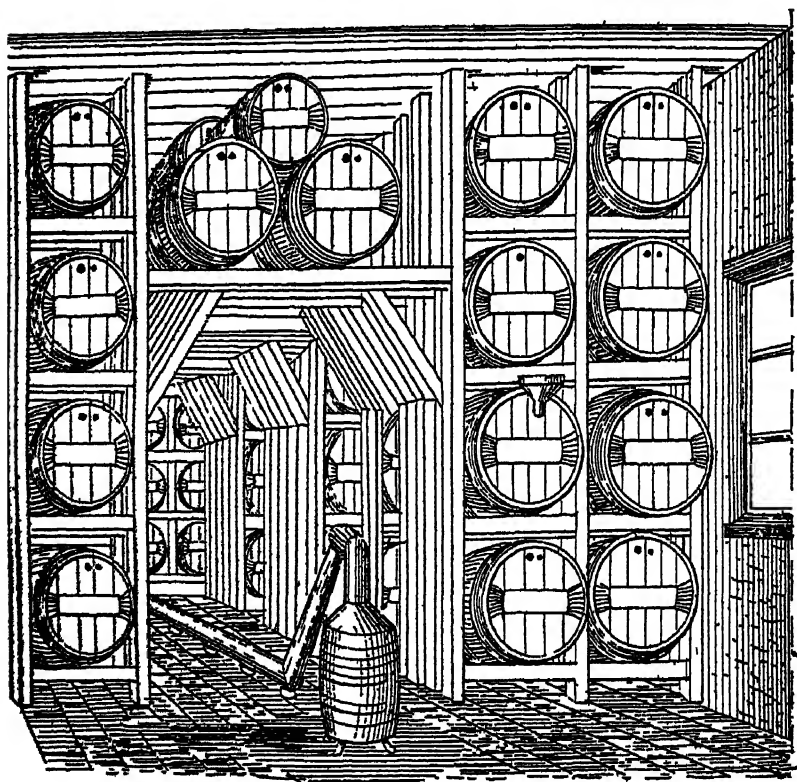


Fig 32—Manufacture of Wine Vinegar, Orleans Process (after *Franche*)

very slow, each cask yielding only 10 litres of vinegar per week, and that in consequence of this it is difficult to eliminate vinegar eels completely from the casks. From time to time the deposit of tartar which forms

within the casks is removed, but this does not take place at sufficiently short intervals for the casks to be sterilised and freed from the eels. Moreover, even when one cask has been cleaned it speedily becomes infected again with eels from its neighbours—a result which is much less likely to happen to acetifiers upon a larger scale. There is also a greater tendency in working with small casks for mother-of-vinegar to form, and to interfere with the acetification.

On the other hand, the slow working of the Orleans process produces the esters to which French vinegar owes its reputation for aroma and flavour.

Notwithstanding the investigations of Pasteur, which showed in what directions the Orleans process could be improved, there has been but little progress in the manufacture. The apparatus devised by Pasteur consisted of large shallow troughs with holes at the side for the admission of air. The amounts of vinegar withdrawn and of fresh wine added were regulated in accordance with the speed of acetification, so that the bacteria always had a sufficient supply of alcohol, and therefore did not attack the acetic acid. The wine was sterilised before acetification to destroy foreign organisms, while the finished vinegar was treated in the same way to ensure its keeping.

**Claudon's Apparatus.**—This plant was devised by Claudon to embody the principles of Pasteur's teaching while being practicable upon a manufacturing scale.

It consisted essentially of a series of superposed shallow fermentation vessels C, C, C, in a square tank, about 6 feet high, which was carried on stone pillars B.

The bottom of each fermentation vessel formed the

cover of the next one, while a floating box of special form was placed in each to keep the bacteria (*Mycoderma*) at the surface of the liquid.

In each fermentation vessel were ten openings E, five on each side, the admission of air through each being controlled by a movable glass panel

The wine was heated to a maximum temperature of  $55^{\circ}\text{C}$  in the vat H, whence it passed into the acetifying

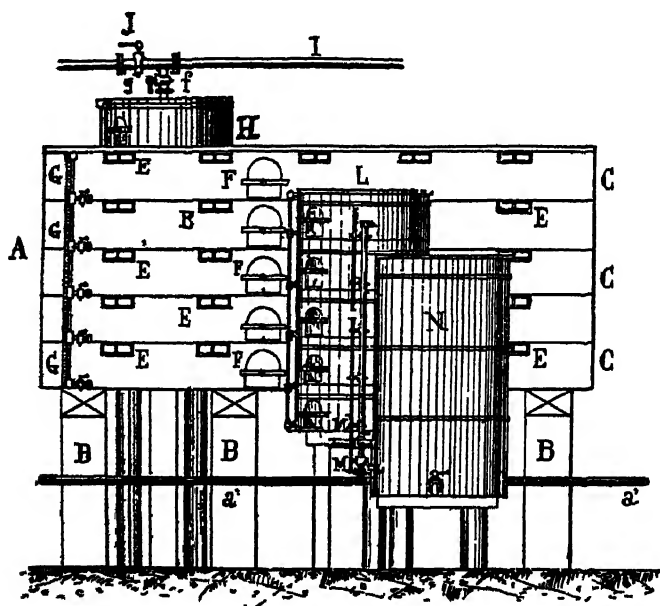


Fig 33.—Claudon's Acetifying Apparatus (after *Franché*)

vessel, while the vinegar was drawn off into the vat L, and filtered through wire gauze filters with wool, which were contained in the vat N. Each tank A worked for about ten days before being cleaned and recharged.

As in the original Orleans process, the alcoholic liquid (gyle) remained quiet, while its surface was exposed to the action of the air, and the advantage of this apparatus

was that the shallow form of the fermentation vessels allowed much more exposure of liquid than was possible in ordinary casks

**The "Quick" Process.**—The general introduction of the so-called "quick" process of acetification is attributed to Schutzenbach, who introduced it into Germany in 1823. In all main essentials, however, the quick process is only a development of the method of acetification used in certain wine-vinegar factories in France in 1670 (see p. 5).

The main difference introduced by Schutzenbach was the use of a vat instead of a cask as an acetifier, with mechanical means for the repeated distribution of the gyle over the acetifying medium.

Until about sixty years ago both processes of acetification were in use in English vinegar works, part of the vinegar being prepared by *fielding*, and the remainder by *stoving*, as it was called.

**English Acetifiers.**—The main differences between English and German acetifiers are that the former are made upon a larger scale than the latter, and as they are used for acetifying an extract of grain rather than an alcoholic wash, must be provided with a larger supply of air.

The acetifiers introduced into British vinegar works, at the time when the 'stoves' replaced the vinegar fields, consisted of large vats taking a charge of 2,000 to 3,000 gallons.

About two-thirds of the way up a perforated false bottom was fixed, and the space above this was loosely packed with raisin stalks or shavings of beech wood, upon which the bacteria developed, while a current of



air was admitted through a number of holes bored in the side of the vat below the false bottom

The gyle was distributed in a fine rain over the shavings by a revolving sparge, and running downwards encountered the currents of air, which enabled the bacteria to acetify a small amount of the alcohol

The liquid collecting in the bottom of the vat was pumped up again into the sparge box, whence it was once more distributed over the shavings, and this process was continually repeated for two to three weeks, until nearly the whole of the alcohol had been converted into acetic acid

When freshly started these acetifiers worked very well, but the shavings soon became clogged by mother-of-vinegar, and where this happened the air was no longer evenly distributed throughout the acetifying medium, but made channels for itself. Hence some parts received an excessive supply of oxygen, whereas in other places there was a deficiency, and the practical result was that part of the alcohol was not oxidised beyond the stage of aldehyde, while another part was oxidised beyond the stage of acetic acid, and was lost

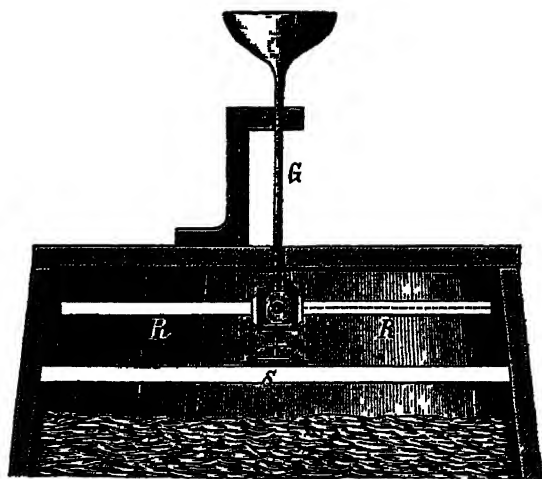
For these reasons shavings were replaced in many vinegar works by wicker basket work. This was much less liable to become clogged than the shavings, and allowed the air to circulate more regularly.

A section of part of an acetifier constructed on these lines is shown in Fig 34

**Distribution of the Gyle.**—One of the most important factors in acetification is the distribution of the wash over the acetifying medium in the finest possible state of division

The most general method of effecting this division is by the use of the sparge. This is frequently constructed upon the same principle as the sparge used in the mash-tun (p. 80), but it is made of vulcanite or block tin, to resist the action of the hot acetic acid.

In the largest acetifiers the sparge is often made of wood, and is in the form of a tapering box pierced by holes at the sides and with an open top to facilitate cleaning at intervals.



G, Supply pipe from pump      R, R, The sparge  
S, Perforated support

Fig. 34 —Section of a Modern Acetifier with Basket Work

Such heavy sparges will not revolve by the force of the escaping liquid, and require to be driven by a cog-wheel, whereas in the case of the light vulcanite sparges the revolution is produced by the force of liquid. This has the advantage that any failure in the action is at once shown by the stoppage of an outside indicator attached

to the sparge. On the other hand, the narrow tubular sparges are much more liable to become clogged with mother-of-vinegar than the large wooden box sparges, from which any accumulation of "mother" is often expelled by the force of the liquid

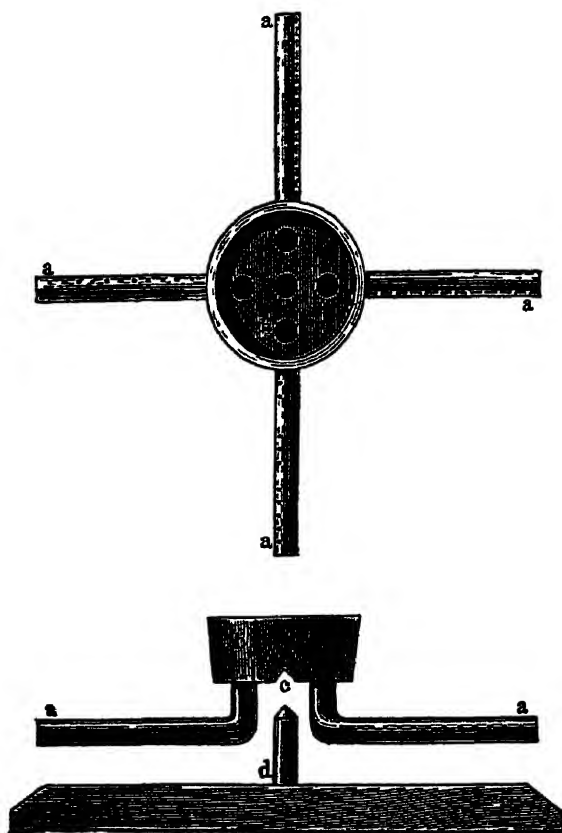


Fig. 35 —Sparge of an Acetifier (*Bronner*)

**The Tipping Trough.**—An ingenious device for distributing the wash over the surface of the acetifying medium is shown in Fig. 36. It consists of a wide-angled trough with a partition in the middle, so as to form the two compartments *a* and *b*. At the angle *c* there is an

axis upon which the trough can swing either to the right or to the left as far as the stops *d*. The wash pumped from the bottom of the acetifier falls through the tap into one of the compartments until this is filled to a certain height. It then tips over and discharges the wash over the surface of the acetifying medium, while the empty compartment is at the same time brought beneath the tap to be filled and discharged in the same way. This process continues alternately, so that each side of the surface of acetifying medium is alternately flushed with a large volume of the liquid.

With small acetifiers this device works admirably, but it is unsuitable for acetifiers of even moderately large dimensions, as the weight of liquid in the compartment is so great that in its sudden fall it produces a great strain on the apparatus.

**Siphon Distributors.**—Another method of distributing the wash is to pump it into a closed tank above the acetifier. In this tank is a siphon tube, the longer limb of which discharges the liquid into a tray pierced with numerous small holes within the acetifier, whence it trickles in fine streams over the shavings or basket work.

The air required in the siphon tank is drawn from the space at the top of the acetifier, so that the aeration of the wash remains under control.

In some apparatus a combination of the siphon tube and sparge is employed with the object of automatically regulating the supply of wash to the acetifier. This

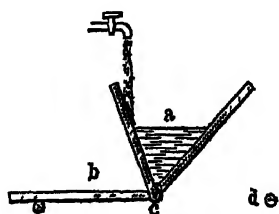


Fig 36—Tipping Trough  
(Brunner)

arrangement is shown in Fig 37 The liquid pumped from the base of the acetifier is delivered into the small cask *c*, through the pipe *b* When it reaches a certain level it is drawn over through the glass siphon *d* into the funnel *e* of the sparge *f*, and is thence distributed by the revolving arms *g, g* The point on which the sparge revolves is shown at *h*, while *i* represents the cover of the acetifier, and *k, k* holes for the escape of the air The flow of the wash into the acetifier can

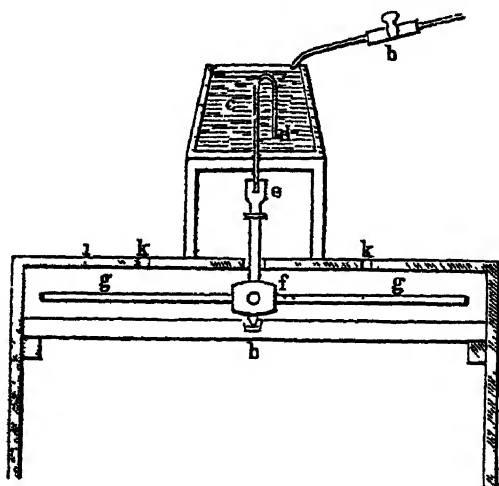


Fig 37 —Combined Siphon and Sparge

thus be readily controlled by regulating the opening of the cock at *b*, and by raising or lowering the siphon tube

**Aeration Devices.**—The most simple method of supplying air to the acetifiers is by piercing a number of small holes in the sides of the vat below the false bottom that supports the acetifying medium

An effective arrangement is to have from 6 to 12 holes with a diameter of about  $\frac{3}{4}$  inch, and it is preferable to

have glass tubes projecting from some of these into the interior of the vat.

The object of this will be seen by reference to the accompanying diagram (Fig. 38), which represents a vertical section of an acetifier. The air entering through the holes at the bottom must tend to rise vertically upwards until it escapes through the openings *b* near the centre of the cover. There will thus be a large cone-shaped area *A*, where the aeration will be less complete than

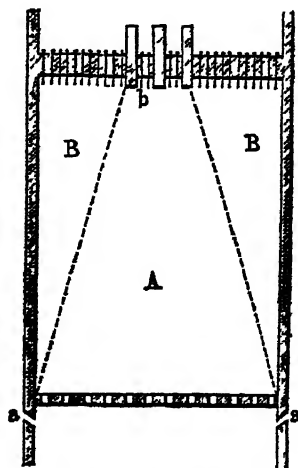


Fig 38—Diagram showing Aeration of an Acetifier

at the outside *B, B*. This less active space becomes larger with the increase in the diameter of the vat, so that for this reason the aeration in small acetifiers is frequently more uniform than in larger apparatus.

By passing tubes a foot or more into the interior through alternate holes, the aeration will tend to become more regular throughout the whole of the acetifying medium.

Another way of aerating the interior is by means of an air tube in the bottom of the acetifier. This projects

upwards nearly to the level of the false bottom, and is protected from the falling vinegar by a conical roof supported on a tripod (Fig 39) The air escaping from

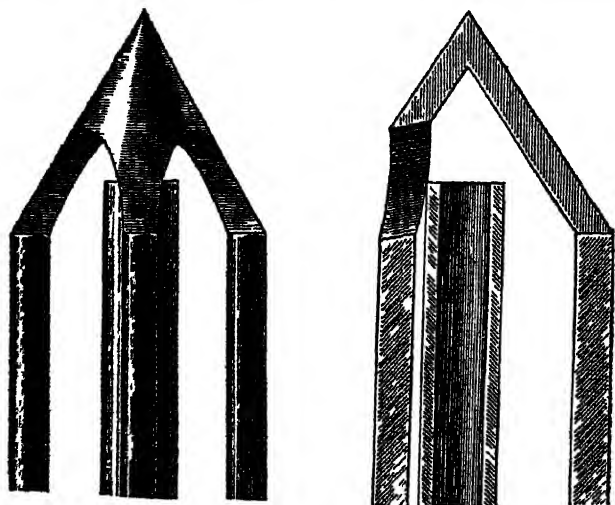


Fig 39 —Aeration Device

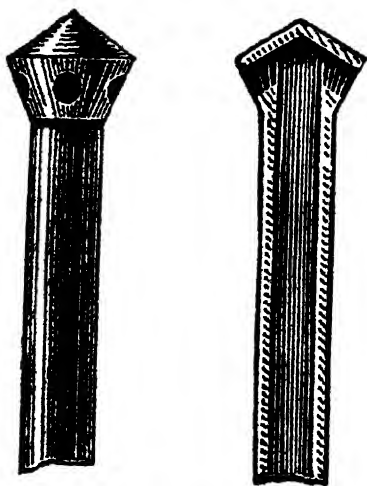


Fig 40 —Aeration Tubes

the central tube is distributed by contact with this roof, and rises through the middle of the acetifier

The same end is effected by an aeration tube of the form shown in Fig. 40, in which holes for the escape of the air are provided beneath the conical cover.

The outlets for the escape of the air should be of larger size than the inlets, and are preferably to be placed near the middle of the cover. Sliding shutters, which can be drawn across the top openings, enable the air supply to be regulated in accordance with the yields of acetic acid obtained from the alcohol in the wash.

Each acetifier will vary in its speed of action and its uniformity of acetification, and it is, therefore, necessary to vary the conditions of aeration in every instance until satisfactory results have been obtained.

The diameter of the outlet openings at the top ought to equal the sum of the diameter of the inlets at the sides.

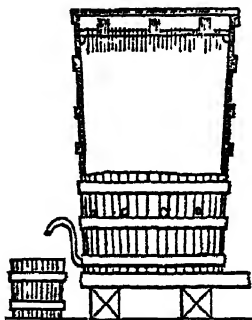


Fig 41—Wagenmann's Graduator

**Wagenmann's Graduator.**—A form of acetifier working by the 'quick process' was devised about 1830 by M. Wagenmann. This consisted of a small oak cask about  $5\frac{1}{2}$  feet high by  $3\frac{1}{2}$  feet in diameter at the top. A series of holes was pierced at about 15 inches from the bottom, for the admission of air, while the liquid to be acetified was poured in through a funnel at the top. At about 5 inches from the lid of the cask a perforated shelf was fixed, and through each of the 400 holes cotton or hemp wick was suspended to guide the liquid downwards on to the beech shavings, with which the acetifier was packed. There were also four larger holes in this shelf,



in which were fixed short glass tubes projecting above and below the wood. These were intended for the escape of the air admitted through the holes below. After acetification was complete the vinegar was drawn off through the siphon tube at the base.

In this *graduato*, with its suspended cords, we have the germ of the idea utilised in Luck's acetifier, in which the acetifying medium consists of bunches of cords stretched between the distributing tray and the false bottom.

**Singer's Apparatus.**—This is composed of a series of rectangular boxes, which are superposed above each other. In each of these is a series of wooden tubes packed with shavings or charcoal, and the wash is made to trickle through these successively from top to bottom, while air is admitted through ventilators at the sides and at the top.

To prevent loss of heat, the entire apparatus is enclosed in a case with glass windows.

It is obvious that the acetification surface is much too small for effective working, and that this apparatus, which is described in most of the foreign text-books, would be quite unsuitable for the manufacture of vinegar on a large scale.

**Bersch's Acetifier.**—An Austrian apparatus, which is claimed to give excellent results in practice, is shown in the accompanying figure (Fig 43). The wash is siphoned over from the trough at the top, and slowly percolates through layers of superposed flat plates with narrow spaces between them.

Although this acetifier is suitable for the acetification of small quantities of an alcoholic wash, such as is used

in Germany and Austria, it could not be effectively used with a malt wash, since the spaces between the plates would become rapidly clogged with mother-of-vinegar.

Theoretically it offers a large superficial area for the growth of the bacteria, but the frequent cleaning that

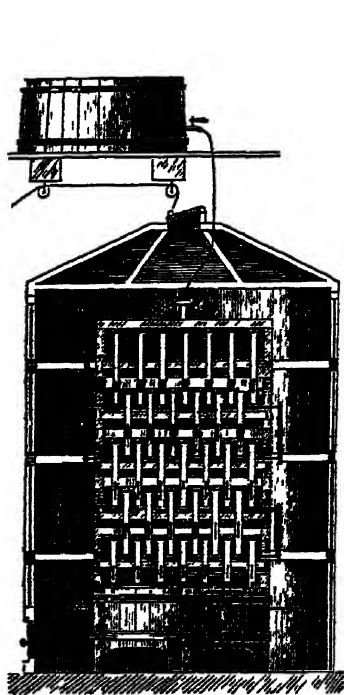


Fig. 42.—Singer's Acetifier

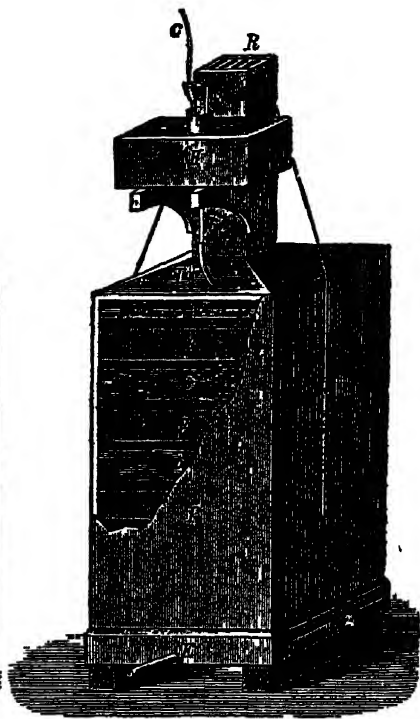


Fig 43 —Bersch's Acetifier

it would require under English conditions of working would render its use unprofitable in this country

### ACETIFICATION IN PRACTICE.

Whatever form of acetifier be employed, the conditions for economical working are essentially the same, and the

superiority of one type of apparatus over another depends upon the extent to which these conditions are satisfied

**Aeration.**—If it were possible always to supply the acetic bacteria throughout the whole of the acetifier with exactly the right amount of air, the conversion of alcohol into acetic acid would under the normal conditions of working be theoretical, but, as a rule, in practice, the aeration process is far from perfect, and considerable losses of alcohol and acetic acid take place owing to the admission of either too much or too little air.

For example, in the old type of acetifiers, packed with beech shavings, the admission of air is by no means uniform throughout the material. In some places, where the mother-of-vinegar has fallen upon the shavings, the air passages become blocked and the acetification is incomplete, while in other places the air will pass more freely, and if present in too large proportion will lead to the oxidation of the acetic acid already formed. Hence all stages of oxidation will be taking place simultaneously in the acetifier, and the total result will be a reduced yield of acetic acid, the deficiency usually ranging from about 10 to 25 or 30 per cent, but sometimes reaching 40 per cent or more.

The substitution of basket work for shavings, as is found in many of the English acetifiers, is a distinct improvement, since it causes the aeration to be more regular, and reduces the tendency to the formation of air channels, but this type of apparatus soon becomes clogged, and requires frequent cleansing if it is to work effectively.

In some of the Continental types of acetifiers,

in which the gyle is made to trickle through tubes, regular aeration is more possible, although some of these apparatus are hardly suitable for working under conditions in which the bacteria produce an excessive quantity of 'mother'

The whole problem of successful acetification depends upon presenting the largest possible surface for the development and aeration of the bacteria in a uniform manner, and of preventing the air passages from becoming clogged through the development of the zoogloal condition of the micro-organisms. The solution of the difficulty is not as simple as at first sight might appear, although some types of apparatus which the writer has had the opportunity of examining under working conditions undoubtedly give results very much nearer to theoretical requirements than do the average acetifiers used in this country

An important factor which must be taken into consideration is the relationship between the economy of acetification and the speed with which the acetifying medium becomes clogged. The better the results obtained in the acetification the sooner will the vat require cleaning, owing to the porous medium becoming clogged. For example, a packing of fine wicker-work will give good results at first, but after a month or so it gradually becomes clogged and begins to work irregularly, and with a greater loss of acetic acid. It will then require cleaning and starting again, which in itself involves a loss of the acetic acid with which the basket work has become impregnated.

The same difficulty attaches to some of the "plate" acetifiers, in which the wash is acetified between

narrow parallel surfaces At first, these work very well, and allow the air to be evenly regulated through all parts of the acetifier, but under English conditions, at all events, they soon become coated with a slimy deposit, and must be cleaned again

Hence it is necessary to regulate the aerating surfaces in an acetifier in such a way that the loss of alcohol involved in working with a more open medium (*e g*, basket work of wider mesh) is more than counterbalanced by the saving in labour effected by the less frequent cleaning of the acetifiers, which is then required

**The Temperature.**—After regulation of the supply of air, the most important factor for the successful working of an acetifier is that the temperature should be kept within definite limits

It has already been shown (p 42) that the *optimum* temperature for the acetification of alcohol varies with different species of bacteria, although in practice it is quite possible to acclimatise the micro-organisms to abnormal temperatures

On the Continent the species of acetic bacteria in common use work best at a much lower temperature than is usual in this country Thus in some of the small German acetifiers the temperature is kept at about 90° to 95° F, and acetification would cease if the temperature rose much above 100° F In England, however, the acetifiers work best at temperatures of about 105° to 110° F, and the temperature can be brought still higher without injuring the bacteria

If small acetifiers providing a relatively large surface for aeration be employed, the temperature will rise spontaneously to the *optimum* point, but with larger

quantities of gyle, or with acetifiers in which the aeration surface is relatively smaller, it is advisable to heat the liquid to about 70° F before starting the acetification process

In the case of the largest acetifiers, taking a charge of 4,000 to 5,000 gallons, it is usual to heat the liquid in the acetifier itself by means of a steam coil at the bottom of the vat. For smaller acetifiers the preliminary heating is conveniently done in a tank (lined with block tin), fixed at a level above a series of acetifiers, into any of which it can be discharged when sufficiently heated.

In the Continental factories the whole of the acetifying room is usually heated by means of a stove, and this course has the advantage that currents of cold air are prevented from entering the acetifiers and causing irregular acetification.

After the initial heating of the gyle in English acetifiers the bacterial oxidation raises the temperature to a point which will depend to a large extent upon the amount of air supplied, so that the daily readings of the thermometers inserted into a hole in the side of the acetifier afford an index of the regularity of the acetification.

If too much air is being supplied, the temperature will rush up very rapidly, and it will then be found that, not only is the alcohol being rapidly acetified, but that the acetic acid produced is also being oxidised.

On the other hand, if the temperature rises very slowly, or even falls, insufficient air to promote the oxidation is being supplied, and the openings must be regulated accordingly.

One advantage possessed by the English in comparison with the Continental process is that the higher temperature

checks the development of vinegar eels and their effects upon the oxidation (p 124)

It is very rarely that these organisms will develop in an acetifier in which the temperature exceeds 100° F, although it is interesting to note that, like the acetic bacteria, the vinegar eel can become gradually acclimatised to higher temperatures. In the case of acetifiers working at about 90° F, it is difficult to prevent their appearance, unless special precautions be taken to use a sterilised wash, and to protect the air-holes of the acetifier.

On the other hand, the high temperatures that are required for rapid acetification cause loss of volatile products, especially aldehyde, through evaporation. To obviate this it is essential to prevent, as far as possible, the escape of air from the acetifying chambers, or stoves," as they are termed by the workmen.

Any outlet for the hot air at the top of the building increases this loss, by allowing the volatile products to escape, instead of being gradually drawn back again into the acetifiers and further oxidised.

**The Group System.**—The strength of vinegar that can be obtained directly from the acetifiers is restricted by the fact that the bacteria are sensitive to the action both of strong alcohol and of acetic acid. Alcohol in the proportion of about 10 per cent kills them, but long before that strength is reached their activity is checked. On the other hand, they offer much greater resistance to acetic acid, and do not reach their full vital activity until the acidity reaches about 2 per cent.

On these facts is based the *group* system of acetification, which consists, in brief, of acclimatising the bacteria to

thrive best under certain conditions of alcoholic and acetic strength

It is not possible to produce a 12 per cent vinegar directly from one acetifier, since the proportion of alcohol required would be fatal to the bacteria. Hence, in the production of concentrated vinegars, such as *Essigsprit*, the acetification is carried out in three groups of acetifiers. The first of these is charged with a wash capable of yielding about 6 per cent of acetic acid. The vinegar leaving these is fortified with an alcoholic wash (usually potato or grain spirit), in sufficient quantity to yield a vinegar of 9 to 10 per cent strength in the second group of acetifiers, while in like manner the vinegar from these is again fortified before being transferred to the third group of acetifiers, where the acetification is completed.

Such a method of working is only possible where a strong alcoholic wash is obtainable.

**Disturbances due to Mother-of-Vinegar.**—However carefully the supply of air to the acetifiers and the temperature are controlled, it is impossible to prevent a gradual accumulation of mother-of-vinegar upon the baskets or porous packing in the vat. When once this "tripe," as the workmen term it, begins to form, the proper supply of air is checked, and under these conditions the growth of the mother-of-vinegar increase still further.

The formation of this remarkable zoogloal condition of the bacteria (see p 34) appears to be promoted by the presence of a limited supply of air.

For example, if a bottle of freshly-made vinegar be tightly corked no alteration beyond a slight deposition of albuminous matter will take place, but if the cork be slightly loosened so that a trace of air gains admission



to the liquid, a succession of solid gelatinous wads will form in the neck, and eventually fall to the bottom. This is commonly described as the vinegar "becoming mothery," and is the cause of occasional complaints. It is completely cured by sterilisation (see p. 132).

**The Vinegar Eel.**—As is mentioned above, one of the greatest troubles with which the vinegar maker has to contend is the minute animal known as the vinegar eel.

There are numerous references to it in scientific literature, one of the earliest being in the Philosophical Essays of Robert Boyle (1661) — "We have made mention to you of a great store of living creatures which we have observed in vinegar, of the truth of which observation we can produce divers and severe witnesses, who were not to be convinced until we had satisfied them by ocular demonstration, and yet there are divers parcels of excellent vinegar wherein you may in vain seek for these living creatures, and we are now distilling some of that liquor, wherein we can neither by candle light nor by daylight discern any of these little creatures, of which we have often seen swarms in other vinegars."

The occurrence of eels in vinegar did not escape the notice of Leeuwenhoeck, who has the following amusing reference to them \* — "I have also described a full-grown live eel, such a one whereof there were many more in the vinegar. I cannot but take notice how some men are deceived that think of the sourness of vinegar proceeds from eels pricking their tongues with their tails, for if this were true, then would some vinegar be flat because there are no eels in it, or rather eels are dead in it, as is usual in cold or frosty weather."

\* *Trans Roy Soc*, 1685, xv, 965

The organism to which these statements refer is the *Leptodera oxophala*, and appears to be identical with the "eels" that will develop in sour paste

It is of very frequent occurrence in Continental vinegar works, where the vinegar is manufactured at a lower temperature than is usual in England. According to Czernat, it may be introduced into the vinegar from the

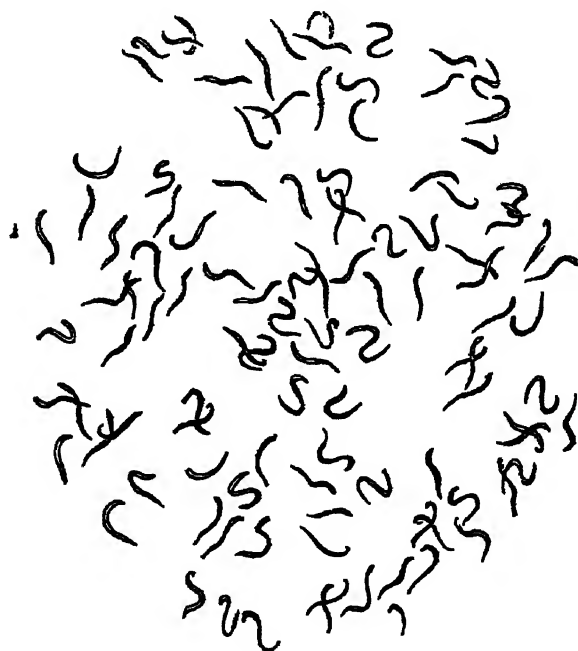


Fig 44 —Vinegar Eels (*Pasteur*)

water, but it is much more probable that it is derived from the air

Occasionally when vinegar is exposed to the air for a short time it will swarm with these creatures, and the same thing may happen in an acetifier, so that every drop of the vinegar has the appearance shown in Fig. 44.

The structure of the vinegar eel is very simple (Fig 45), the body is cylindrical, and ends in a sharp point, and the skin, which is changed from time to time, is smooth, structureless, and very strong. According to Czernat's average measurements, the length of the male's body is about  $\frac{1}{15}$  inch, and that of the female about  $\frac{1}{16}$  inch.

Vinegar eels move either backwards or forwards, and progress by alternately shaping themselves into an S and straightening out again. They appear to be incessantly darting through the vinegar in all directions, but always with a tendency towards the surface, for they are air-breathing animals.

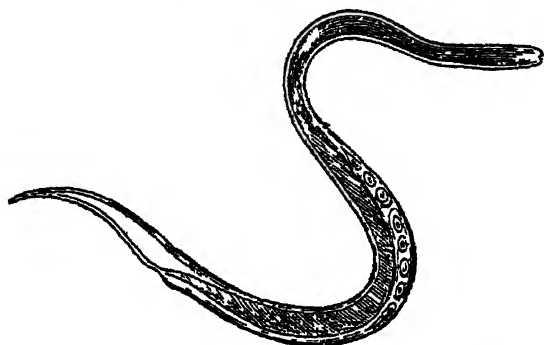


Fig 45 —Vinegar Eel, highly magnified (*Pasteur*)

They are capable of living in very dilute alcohol or acetic acid, as well as in vinegar, and can resist great variations in temperature, not being killed until the temperature reaches 140° to 150° F in one direction or 22° F in the other.

Pasteur\* was the first to point out how harmful the vinegar eel was in the manufacture of vinegar. Should they develop within an acetifier a struggle for air begins

\* *Loc cit*

between them and the acetic bacteria. For a time a working balance may be struck between them, and the air shared, but during this struggle, which may last for weeks, the activity of the bacteria is impaired, and though the conversion of alcohol into acetic acid still proceeds, it does so with an increased expenditure of time and a reduced yield.

Should the vinegar eels gradually obtain the upper hand, they interfere more and more with the working of the apparatus, and eventually the acetification comes to a standstill. If, on the other hand, the bacteria get the mastery, they tend to deposit 'mother' on the surface of the liquid, as the result of their obtaining insufficient oxygen. This skin effectually prevents the eels from breathing when they come to the surface, and so they perish and fall to the bottom of the acetifier, where they accumulate as a white deposit and may putrefy. In either case the only remedy is to clean and disinfect the apparatus and start afresh.

It was only with difficulty that Pasteur could convince certain French vinegar makers of the advantage of getting rid of the vinegar eel, for so general had it become with them that they had begun to look upon it as an essential part of the process instead of a deadly enemy.

Even after vinegar containing eels has been freed from them by filtration the ova remain, and under suitable condition will develop into eels, which will rapidly multiply and make the vinegar appear turbid, though without materially affecting its acetic strength. This after-development of eels is easily prevented by heating the vinegar to 160° F in a sterilising apparatus, as described on p. 133.

**The Vinegar Mite.**—Another enemy of the acetic bacteria is known as the "vinegar mite." When once it obtains a footing within an acetifier it multiplies rapidly, interferes with the oxidation, and is not easily exterminated. Beisch records a case that came under his observation. The vinegar made in a certain Italian factory swarmed with these mites, which had finally brought the acetification to a complete standstill. The manufacturers attributed their presence to the soil below the acetifiers, but had no idea that they pointed to a want of care.

It is through the aeration holes in the acetifiers that the mites gain access to the apparatus, and attempts have been made to prevent this by placing bird-lime round the outside of the holes, while in some of the more recent patents fine wire gauze is used for the same purpose.

At first the acetic bacteria do not appear to be much affected by the presence of the mites, but as these increase and then die and fall to the bottom their dead bodies begin to putrefy, and the putrefactive bacteria will sooner or later master the acetic bacteria.

The vinegar in which the mites have gained the upper hand has a peculiar yellowish shade, and contains what appear to the naked eye to be fine white specks.

When examined under the microscope these have the appearance shown in Figs 46 and 47.

These two forms, apparently those of the male and female, are always present. They appear to belong to the class of *Sarcoptidae*.

When once vinegar mites have become established within an acetifier, they can only be expelled by destroying

them simultaneously with the acetic bacteria. For this purpose the vat must be emptied, and the interior thoroughly washed with hot water, then well fumigated with

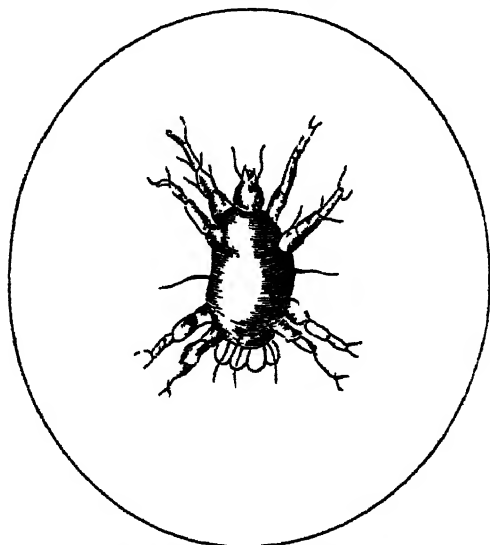


Fig. 46 — Vinegar Mite (*Bersch*).

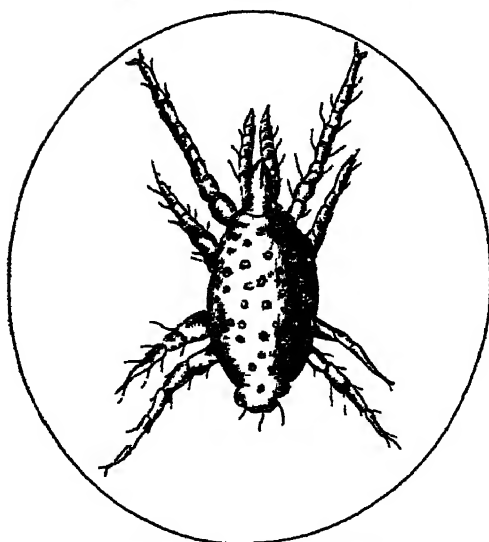


Fig. 47 — Vinegar Mite (*Bersch*).

burning sulphur until all life is destroyed, and again washed. It is then recharged with gyle and a little crude vinegar containing the bacteria, but it will be some time before the acetifier gets into working condition again.

**The Vinegar Fly.**—The vinegar fly (*Drosophila funebris*) is of very common occurrence, and may be observed in any vinegar works during the hotter months of the year. It is about one-tenth of an inch in length, and is characterised by its large red eyes, red thorax, and red legs. The abdomen is black with yellow stripes, and the wings are somewhat longer than the body. According to Brannt, the larva is white, has twelve segments to its body, and four wart-like structures on the back. After eight days it is transformed into a yellow chrysalis.

Vinegar makers are not in the habit of paying much attention to the presence of the vinegar fly, since, so far as is known, it does not in any way affect the manufacture, and it is readily prevented from becoming a nuisance by keeping the works thoroughly clean and not allowing any spilt vinegar to lie about upon the ground.

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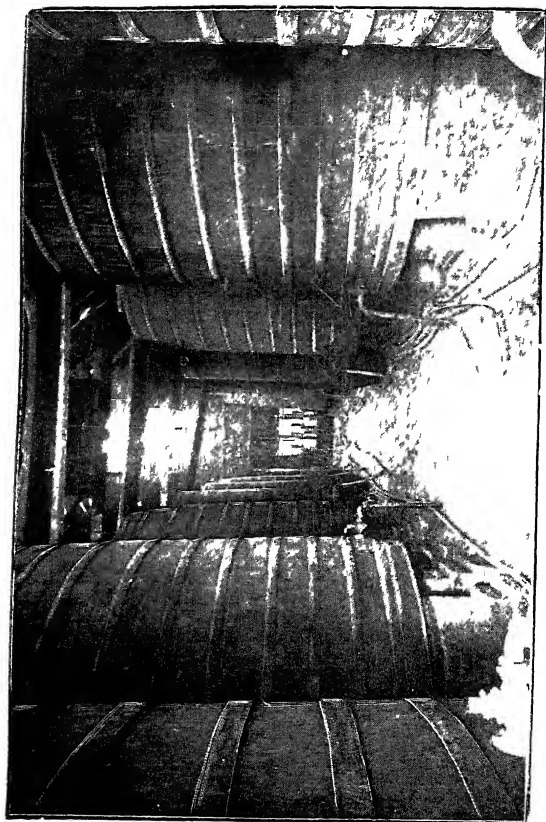


Fig 48 —The Rape Shed

## CHAPTER VIII

## TREATMENT OF THE CRUDE VINEGAR.

Filtration—Clarification—Action of Ferrocyanide—Sterilisation—Storage—  
Distillation—Composition of the Residue in the Still

**Filtration of Vinegar.**—After leaving the acetifiers, the crude vinegar is pumped into store vats, where it is allowed to remain for several weeks or months to mature. During this storage period it deposits albuminous matter, bacterial cells, etc., and undergoes partial clarification. In fact, the longer the vinegar can be stored the more readily can it subsequently be made sufficiently "bright" for sending out. The filters used in vinegar factories are technically known as 'rapes,' owing to the fact that raisin stalks or rapes were first used for the purpose in the seventeenth century (see p. 6). The spent raisin skins left as a residue in the manufacture of British wines are still sometimes used for this purpose, although as a rule the filter bed is generally composed of other filtering media, such as beech chips, in conjunction with layers of shingle, sand, or kieselguhr.

Paper pulp is also used for filtering vinegar, and has the advantage of yielding a brilliant filtrate, although it soon becomes clogged, and offers difficulties in the case of vinegar which has not been stored for a long time.

The general appearance of the inside of a "rape" shed is shown in Fig. 48.

The large vats, each of which takes a charge of about 3,000 to 4,000 gallons, are arranged in rows down the sides of the shed, and each is provided with its own pump, and mains, so that the vinegar can be pumped into any of them at will

The filtering medium is supported upon a false bottom some distance up within the vat, so that a vertical section of a 'rape' shows two layers of liquid separated by the filtering medium

It is a common practice for the "rapes" to be worked in groups. The vinegar from the store vats is introduced into the first group, and is there continually pumped over and over, until it is bright enough to be passed on to the second group of rapes. There the same process is repeated until the vinegar is nearly brilliant, and the filtration is then completed in the third group of rapes, which should yield a product described by the workmen as "candle-bright"

When the vinegar has been brewed from a low-dried malt, or when much raw grain has been used, it is extremely difficult to remove the last traces of suspended matter, and the vinegar will continue for a long time to show a characteristic silken opalescence, which might escape notice in ordinary daylight, but is very obvious when the bottle is held up to an artificial light

**Clarification of Vinegar.**—The persistent cloudiness which occurs in certain vinegars is sometimes more rapidly removed by a process of clarification than by filtration. The methods employed are sometimes mechanical and sometimes chemical. In the first case an insoluble substance, such as Spanish earth or kieselguhr, is stirred up with the vinegar, and as it subsides it carries

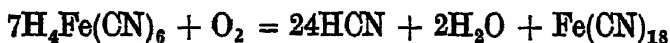
down with it the albuminous particles to which the turbidity is due.

In the chemical methods the albuminous substances may be precipitated by the addition of a gelatinous agent, such as isinglass, or a measured quantity of a solution of potassium ferrocyanide may be added

**Precipitation with Ferrocyanide.**—This reagent will precipitate, not only a portion of the nitrogenous compounds, but also any iron in the vinegar, and the vats in which the precipitation is carried out are usually stained dark blue from the formation of Prussian blue

It is essential, however, that no excess of ferrocyanide should be used, and on more than one occasion vinegar containing such excess has caused a bright blue colour to appear in pickles which had been preserved in brine containing a trace of iron.

The behaviour of potassium ferrocyanide in vinegar was investigated by Harden\* It was found that the oxidation which took place spontaneously in an aqueous solution of potassium ferrocyanide also occurred when the salt was dissolved in dilute (6 per cent) acetic acid, a deposit of Prussian blue being formed, while hydrocyanic acid was liberated in accordance with the equation—



The hydrocyanic acid thus produced disappeared very slowly from the acetic acid, the amount being but slightly reduced after the liquid had stood for a month.

When, however, the ferrocyanide was added to vinegar, some further reaction apparently took place, for although the deposit of Prussian blue was obtained, it was not

\* *Dr Hamill's Report to L.G.B.*, 1908, p. 27.

possible to detect hydrocyanic acid in the filtrate from that deposit. Possibly it had entered into combination with the aldehyde of some other constituent of the vinegar, and this explanation of the failure to detect it received support from the results of experiments, which showed that hydrocyanic acid did actually combine with some substance in vinegar to form an unstable compound, which was decomposed when the vinegar was heated.

Although no definite proof was obtained of the formation of hydrocyanic acid when an excess of ferrocyanide was added to vinegar, the evidence pointed to its production, and justified the conclusion that such vinegar should be looked upon with suspicion.

**Sterilisation of Vinegar.**—After filtration or clarification, vinegar will still contain acetic bacteria or their spores, and when exposed to the air will soon become coated with a zoogloal film. When the vinegar is sent out in casks, and the consumers allow air to gain access to it, by not replacing the spigot, this growth of the bacteria will occur upon the surface and make the liquid turbid. In other words, the casks become "mothery." The same thing happens in the case of bottled vinegar when the stopper is defective and allows air to enter the bottle.

Long continued storage of the vinegar before sending out will check this growth of "mother," as a large proportion of the bacteria will die when the vinegar is kept for some months in a well-closed vat. Want of space, however, may prevent this from being practicable in many cases, and at best it is not as effectual as sterilising the vinegar.

As all the species of acetic bacteria perish at a

relatively low temperature, it is sufficient to heat the vinegar to  $150^{\circ}$  F, to insure its keeping, even when exposed to the air, since the acetic acid will prevent the development of micro-organisms from without. This process of sterilisation is most simply effected by passing the vinegar through a coil surrounded by a tank of water, which can be heated by steam to the sterilising temperature. On leaving this heating tank the vinegar is passed through one or (preferably) two other coils chilled by a current of cold water, and is thus cooled down nearly to the normal temperature, and leaves the sterilising apparatus without any appreciable loss of acetic acid.

The construction of the steriliser will be understood by reference to the accompanying diagram, in which A represents the feeding tank into which the vinegar is pumped, to give it sufficient height to flow through the apparatus. The heating tank is shown at B, and the cooling tanks at C, the temperature of the vinegar as it leaves B and G being indicated by thermometers in the vinegar main at the points *e* and *f*.

The flow of vinegar is regulated by the cock *g*, until the temperature shown at the point *e* is not less than  $150^{\circ}$  F. while the temperature of the vinegar leaving the cooling tank should not exceed  $70^{\circ}$  to  $75^{\circ}$  F at the point *f*.

Sterilisation in this way causes a slight deposition of albuminous matter after the vinegar has stood for some time, and for this reason it is advisable to run the sterilised vinegar into storage vats, and to leave it for a few days before bottling. This is not so important in the case of cask vinegar, since the slight deposit will not be noticeable, and when once it has subsided does not affect the permanent brightness of the liquid.

In addition to its action in improving the keeping qualities, sterilisation has also the effect of maturing the vinegar, and of giving a softer taste and less acid aroma. It is probable that this is due to its promoting the combination of the residual alcohol in the vinegar with the acetic acid, and thus accelerating the forma-

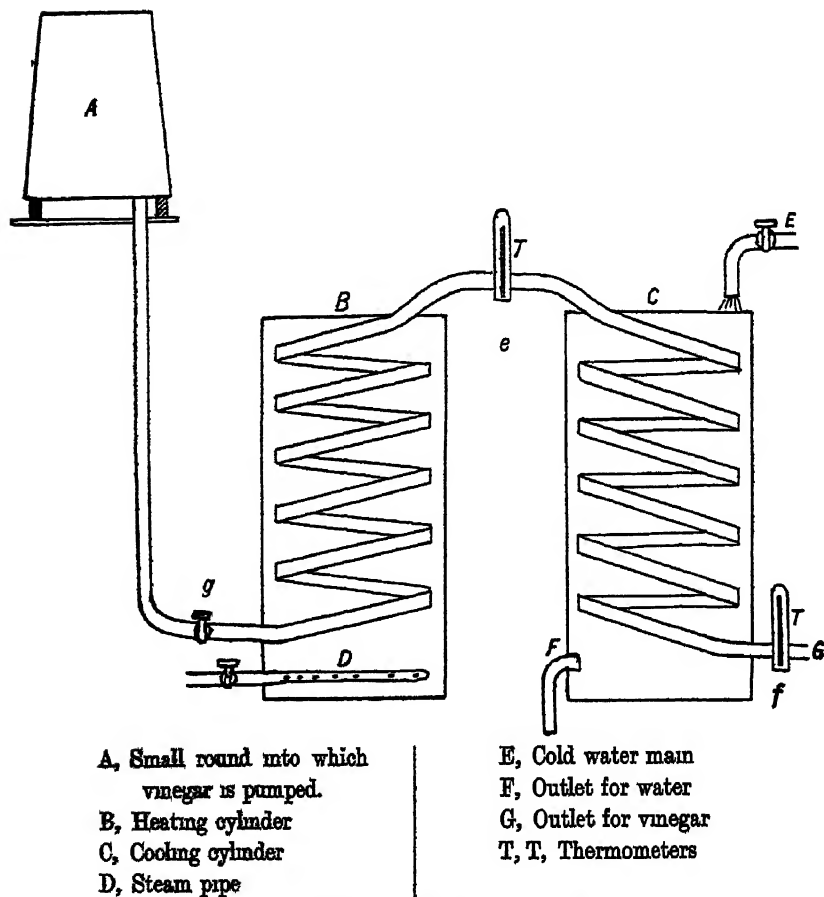


Fig 49 —Diagram of Sterilising Apparatus

tion of the esters to which matured vinegar owes its flavour.





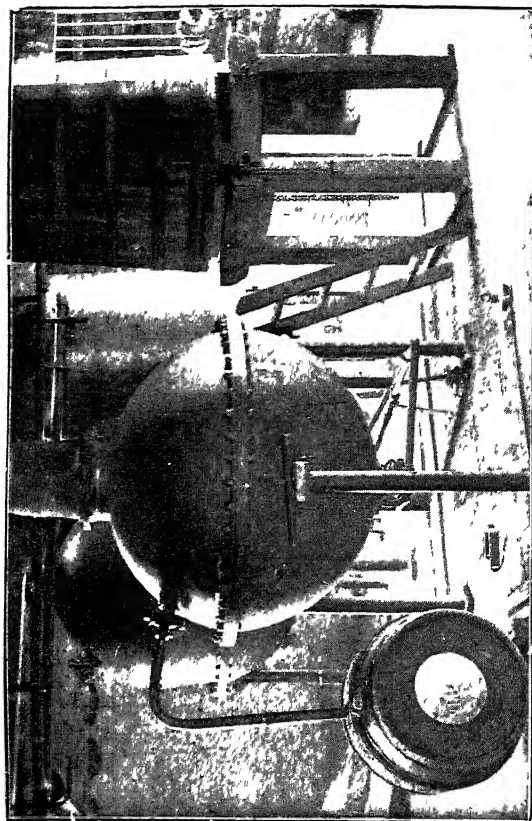


Fig 50 —Vnegai Still

**Distillation of Vinegar.**—The early method of distilling vinegar to obtain *aromatic* or *radical* vinegar has already been described (p. 63). The drawback to a simple distillation at the ordinary pressure is that it is not possible to expel the acetic acid without at the same time overheating the solid matter in the vinegar, so that empyreumatic products are also distilled. Hence the early process was not economical, for a large proportion of the acid had to be left behind with the residue in the still.

In the modern process the vinegar is distilled at a lower temperature under reduced pressure, and the distillation can then be carried very much further without any risk of burning the solid residue.

The small stills commonly used take a charge of about 100 gallons of vinegar. They are made of tin, and are heated by a steam jacket. The outlet pipe of the still is connected with a coil immersed in a tank of running water, and this delivers into a receiver, in which is a pipe connected with a vacuum pump. Distillation is effected at a reduced pressure of 15 to 20 inches, and is continued until the still contains only a semi-solid mass resembling treacle. Fig. 50 shows one of the vinegar stills used in the works of Messrs. Beaufoy & Co.

By interrupting the distillation at definite points it is possible to obtain distillates of considerably higher strength than the original vinegar. For example, if a 6 per cent. vinegar be distilled, the first third of the distillate will contain about 3 per cent. of acetic acid, the second third about 5.5 per cent., and the final third between 9 and 10 per cent.

The residue will also retain a small proportion of

acetic acid, while the other constituents of the malt and grain will be present in a concentrated form. The still residue, in short, is a dark malt extract, slightly acid, and devoid of any diastatic capacity.

Analyses of two samples of still residues made by Allen \* gave the following results —

	From Bailey Vinegar	From Rice and Grain Vinegar
Total solids,	Per cent 43 20	Per cent 72 30
Ash, .	8 38	9 21
Alkalinity of ash ( $K_2O$ ), .	2 07	1 40
Phosphoric acid,	2 67	0 24
Nitrogen,	2 63	2 63

The distillate is sold under the names of *distilled malt vinegar*, *white vinegar*, and *white wine vinegar*, while it has been held by a Sheriff in Fife that distilled malt vinegar may legally be sold as “malt vinegar”

\* *Analyst*, 1893, xviii, 241

## CHAPTER IX

## METHODS OF EXAMINATION.

DETERMINATION OF ACIDITY—Automatic Supply Burette—Standardisation of Alkali Solutions—Salleron's Acétimètre—Otto's Acetometer—Standards of Acidity—Crude Pyrohgneous Acid—TOTAL SOLIDS—Alkalinity of the Ash—MINERAL ACIDS—Detection—Determination—Combined Sulphuric Acid—Methyl-acetol—FORMIC ACID—TOTAL NITROGEN—Nitrogenous Compounds—PHOSPHORIC ACID—INOSITOL IN WINE VINEGAR—COLOURING MATTERS—Measurement of Colour Intensity—Lovibond's Tintometer—Caramel—Cochineal—Archil—METALLIC IMPURITIES—Iron—Copper—Lead—Tin—Arsenic—Official Method of Testing for Arsenic

**Determination of Acidity.**—The acidity of most ordinary vinegars may be accurately determined by titration with standard sodium hydroxide solution, with phenolphthalein as indicator. In the case of very dark samples dilution is necessary, or the caramel may be precipitated with fuller's earth, and an aliquot part of the filtrate titrated. 'Spotting' tests with litmus paper as indicator have been shown by Brode and Lange\* to give results about 1 per cent. lower (in terms of  $\frac{N}{2}$  alkali solution) than direct titration with phenolphthalein as indicator. Hence, litmus is less reliable than phenolphthalein as an indicator for vinegar.

Where numerous samples require titrating every day, as in checking the working of acetifiers, it is advisable

\* *Arbeit Kaiserl Gesundheitsamt*, 1900, xxx., 1

to use a special stock alkali solution, with an automatic-supply burette, with a guard to prevent absorption of carbon dioxide

**Standardisation of Alkali Solutions.**—The most rapid method of standardising an alkali solution is by the use of pure oxalic acid. The ordinary pure chemical usually requires further purification for this purpose. This may be readily effected by shaking the crystals with warm water in insufficient quantity to dissolve them completely, filtering the solution, and leaving the filtrate to crystallise. The new crop of crystals is dried with filter paper at the ordinary temperature, and kept for use as an original standard.

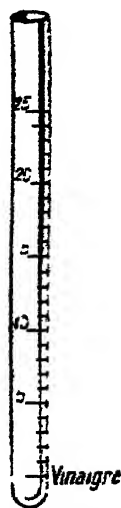


Fig. 51  
Salleron's  
Acétimètre.

**Salleron's Acétimètre.**—The instrument used by the French excise officials (and by the Customs officers in Mauritius) for estimating the acetic strength of vinegar is a simple glass tube closed at one end and graduated into divisions. The first of these, starting from the bottom, is marked with the word "*Vinaigre*," and indicates the quantity of vinegar (4 c.c.) to be taken for the test.

This quantity of vinegar is introduced by means of a 4 c.c. pipette, a drop of phenolphthalein solution added, and then successive small quantities of a standard solution of sodium hydroxide,\* the tube being closed with the thumb and shaken each time until a permanent pink coloration is obtained after the addition

\* Twenty c.c. neutralise 4 c.c. of dilute sulphuric acid (100 grammes of monohydrated acid diluted to 1,000 c.c.).

of a single drop. The strength of the vinegar may then be read directly upon the scale. For acids above 25 per cent in strength corresponding dilution is necessary.

An instrument of a similar kind known as Otto's acetometer, is used by the Customs officials in Germany, while a more accurate tube has been devised by Dujardin.

This method of determining the acidity of vinegar is only capable of giving rough estimations, although, on the whole these are much nearer the truth than the results given by the old acetometer of the British Excise (p 15).

**Standards of Acidity.**—The standard for the minimum strength of vinegar adopted in 1877 by the Society of Public Analysts has already been mentioned (p 61). Although this limit had no legal sanction, it was generally accepted by the trade, and convictions for "watering" were from time to time obtained for the sale of vinegar containing less than 3 per cent. of acetic acid.

In May, 1912, the Local Government Board recommended that no vinegar or artificial vinegar should be sold containing less than 4 per cent. of acetic acid.

Since the Local Government Board has no power, without fresh legislation, to fix standards, it is questionable whether the action taken by certain public authorities against the vendors of weaker vinegars would be supported if an appeal were made from the convictions obtained in several instances.

So clearly is this recognised in some quarters that certain boroughs have refused to prosecute the vendors of weak vinegar, and have urged that combined action should be taken in petitioning for the necessary powers to be conferred upon the Local Government Board.

Several of the Colonies have fixed limits for the strength of the vinegars which may be sold within their jurisdiction

The question of strength is also taken into account in charging duties upon vinegar imported into the different countries, and is thus frequently brought to the notice of English manufacturers

A list of the principal Colonial tariffs for vinegar and acetic acid will be found in Appendix I

**Estimation of the Strength of Pyroligneous Acid.**—The titration of crude pyroligneous acid presents considerable difficulty, owing to the deep colour of the liquid preventing the end-point of the reaction being seen

The strength may be approximately estimated by Mohr's method, in which a weighed quantity of the acid is stirred with a weighed quantity of barium carbonate until effervescence stops, after which the undissolved barium salt is separated, washed, dried, and weighed. The acids will correspond to the amount of barium carbonate dissolved, and are calculated as acetic acid. Or the undissolved carbonate may be determined by titration with standard nitric acid

**Total Solid Matter.**—Usually a measured quantity (10 c.c.) of the vinegar is evaporated on the water-bath with frequent shaking, and the residue dried in the water-oven until constant in weight. The shaking of the dish during the evaporation accelerates the expulsion of the acetic acid, which is obstinately retained by the solid matter. Thus, it was shown by Brode and Lange\* that a wine vinegar when evaporated without shaking left a residue of 0.79 per cent. containing 0.2 per cent. of acetic acid, while when the dish was frequently shaken

\* *Arbeit Kaiserl. Gesundheitsamte*, 1909, xxx, 1

the residue was 0.64 per cent, and contained only 0.08 per cent of acid.

In any case, titration of the acidity of the residue and deduction of the result from the amount obtained by weighing is a necessary correction

An approximate estimation of the total solids, accurate within about 0.1 per cent, may be rapidly made by titrating the acidity, and determining the specific gravity of the vinegar at 15° C by means of a standard Bates' saccharometer

From the specific gravity thus indicated the amount corresponding to the acetic acid strength at 15° C is found by reference to Oudemanns' table (p. 75)

The difference will show the specific gravity due to the solid extract from the wort, and the amount of the latter may be found by reference to the subjoined table (p. 142), which is abridged from Schultze's long table

The following example may be given by way of illustration —

A sample of malt vinegar had a specific gravity of 1.014 at 15° C and an acidity of 4.5 per cent. This degree of acetic acid corresponds to a specific gravity of 1.006, while the specific gravity due to the solid extract is  $10.14 - 0.006 = 1.008$ . A specific gravity of 1.008 represents 2.09 per cent of total solids in Schultze's table, while the amount determined by evaporation was 2.07 per cent

**Alkalinity of the Ash.**—In some cases an indication of the probable origin of a vinegar may be obtained by determining the alkalinity of the ash, since in a vinegar brewed from glucose the mineral acid used for the hydrolysis will have combined with part of the bases, and thus cause the proportion of potassium oxide to be low



SCHULTZE'S EXTRACT TABLE

Specific Gravity at 15 c c	Extract in 100 Grms	Extract in 100 c c	Specific Gravity at 15 c c	Extract in 100 Grms	Extract in 100 c c
	Grms	Grms		Grms	Grms
1 0001	0 03	0 03	1 0125	3 23	3 27
1 0005	0 13	0 13	1 0128	3 30	3 34
1 0010	0 26	0 26	1 0130	3 35	3 39
1 0015	0 39	0 39	1 0133	3 43	3 48
1-0020	0 52	0 52	1 0135	3 48	3 53
1 0025	0 66	0 66	1 0138	3 56	3 61
1-0030	0 79	0 79	1 0140	3 61	3 66
1-0035	0 92	0 92	1 0143	3 69	3 74
1-0040	1 05	1 05	1 0145	3 74	3 79
1-0045	1 18	1 19	1 0148	3 82	3 88
1 0050	1 31	1 32	1 0150	3 87	3 93
1 0055	1 44	1 45	1 0153	3 95	4 01
1-0060	1 56	1 57	1 0155	4 00	4 06
1 0065	1 69	1 70	1 0158	4 08	4 14
1-0070	1 82	1 83	1 0160	4 13	4 20
1-0075	1 95	1 96	1 0163	4 21	4 28
1-0080	2 07	2 09	1 0165	4 26	4 33
1-0085	2 20	2 22	1 0168	4 34	4 41
1-0090	2 33	2 35	1 0170	4 39	4 46
1-0095	2 46	2 48	1 0173	4 47	4 55
1-0100	2 58	2 68	1 0175	4 53	4 61
1-0105	2 71	2 74	1 0180	4 66	4 74
1-0110	2 84	2 87	1 0185	4 79	4 88
1-0115	2 97	3 00	1 0190	4 93	5 02
1-0120	3 10	3 14			

In the United States' official definition of malt vinegar it is enacted that the ash from 100 c c of the sample shall require for its neutralisation not less than 4 c c of decinormal acid

Actual determination of the potassium oxide as practised by Tatlock usually affords a more satisfactory criterion than the titration of the ash.

The variations in this figure in different kinds of vinegar

may be illustrated by the following results given by Allen \* —

	Grain and Malt	Grain and Sugar	Rice	Sugar
Alkalinity as $K_2O$ per 100 parts of vinegar,	0.091 to 0.118	0.03	0.013	traces

### DETECTION OF FREE MINERAL ACIDS

**Hilger's Method.**—Free mineral acids in vinegar may be detected by means of a solution of methyl violet (0.1 gm. per 1,000 c.c.), which is not affected by acetic or other organic acids, but is changed to blue or green by mineral acids. The test is best applied by adding 4 to 5 drops of the reagent to 20 c.c. of the vinegar, shaking the tube and comparing the colour with that obtained with dilute acetic acid coloured to the same intensity with caramel.

Congo-red paper is also useful as a preliminary test, being changed to blue by free mineral acids, though it is not affected by acetic acid.

### DETERMINATION OF MINERAL ACIDS

**Hilger's Method.**—Twenty c.c. of the vinegar are neutralised with N/alkali solution, with turmeric paper as indicator, and evaporated to about 2 c.c., and the residue is mixed with a few drops of a 0.01 per cent solution of methyl violet 2B and 4 c.c. of water. The liquid is heated to boiling point, and titrated with N/sulphuric acid until the colour changes to blue or green. It is

\* *Analyst*, 1894, xix, 15.

advisable to compare the change of colour with that given by an aqueous solution of the methyl violet containing about the same quantity of caramel as the vinegar in question

The difference between the number of c c of N/alkali solution originally used and the number of c c of sulphuric acid required in the last titration corresponds to the amount of free mineral acids present The result multiplied by 1 225 gives the percentage in terms of sulphuric acid

### FREE SULPHURIC ACID IN VINEGAR

The amount of free sulphuric acid (0 1 per cent ) which was expressly permitted to be added to vinegar by the Act of George III of 1818 was often considerably exceeded Thus, in the year 1852, a body of Commissioners appointed by the *Lancet*\* examined 27 samples of vinegar typical of the products of the principal manufacturers in this country The samples of only two makers were found to be quite free from sulphuric acid, while the others contained from 0 63 to 6 02 parts per 1,000.

These figures, however, included sulphuric acid present in the form of sulphates, the proportion of combined acid ranging from 0 44 to 0 39 part per 1,000, so that many of the samples were well within the legal limit for free acid.

At the present time it is improbable that any manufacturer in this country adds free sulphuric acid to his vinegar, although, as may be gathered from Muspratt's †

\* *Lancet*, Aug 28, 1852

† *Dictionary of Chemistry*, 1860, p 16

account, the practice died very slowly. It is perhaps hardly necessary to add that vinegars of sufficient acetic strength will keep quite well without any such addition.

**Hehner's Method.**—A method of detecting and estimating free sulphuric acid and other mineral acids in vinegar was based by Hehner\* upon the fact that potassium and sodium acetates (or tartrates) are always present in vinegar. If a small amount of a mineral acid is added, it will decompose a corresponding quantity of acetate or tartrate, with the liberation of the organic acid, but if added in excess of the corresponding quantity of organic salts this excess will remain as a free acid. Hence, vinegars that contain acetates or tartrates cannot contain a free mineral acid, and since on igniting these organic salts they are decomposed into carbonates, an examination of the ash of the vinegar may afford an indication of the presence of free mineral acid.

If the ash is alkaline, it is probable that no free mineral acid has been present in the vinegar, although a quantity insufficient to decompose the whole of the acetates or tartrates might originally have been added, and it is possible for calcium sulphates or other calcium salts to be decomposed in the ignition, and to render the ash alkaline, but if the ash is neutral the presence of free mineral acid is probably indicated.

**Estimation of Free Acid.**—Hehner's method will also give quantitative results. Fifty c c of the vinegar are evaporated with 25 c c of  $\frac{N}{10}$  sodium hydroxide solution, and the residue charred at a low temperature, mixed with 25 c c of  $\frac{N}{10}$  sulphuric acid, boiled, filtered, and washed. The filtrate is titrated with  $\frac{N}{10}$  sodium hydroxide.

\* *Analyst*, 1877, 1, 105.

solution, with litmus or cochineal as indicator. The number of c.c. of alkali required corresponds to the free mineral acid.

Owing to the necessity of repeating the estimation if the amount of alkali originally added was insufficient, Allen and Bodmer\* modified the test by neutralising the whole of the acid present in the vinegar prior to the evaporation.

In the case of vinegars, such as those derived from malt or grain, which contain a large proportion of phosphate, it is necessary to take into consideration the fact that any phosphoric acid liberated in the test will react with alkali (methyl-orange as indicator) in a different way than hydrochloric or sulphuric acid. The importance of this point has been emphasised by Richardson and Bowen†

On boiling potassium phosphate,  $K_3PO_4$ , with a definite excess of sulphuric acid, potassium sulphate and phosphoric acid are produced, but on titrating the excess of sulphuric acid, different results are obtained when methyl-orange and phenolphthalein are used as indicators.

The end point of the reaction is reached, with methyl-orange as indicator, when dihydrogen potassium phosphate has been formed—i.e., only one-third of the phosphoric acid present is shown. On now adding phenolphthalein the titration can be continued until dipotassium hydrogen phosphate is formed, accounting for another third of the phosphoric acid.

**Richardson and Bowen's Method.**—Based upon these considerations, Richardson and Bowen (*loc cit*) have devised the following process, which estimates, not only

\* *Analyst*, 1878, III, 268

† *J. Soc. Chem. Ind.*, 1906, XXV, 836

the sulphuric acid present as such, but also the phosphoric acid liberated from the phosphates by the sulphuric acid. Although part of the phosphoric acid is present as calcium phosphate, no material error is introduced by basing the calculation upon potassium phosphate

Twenty-five c c of the vinegar are evaporated to dryness with 25 c c of  $\frac{N}{10}$  sodium hydroxide solution, and the residue charred at a temperature insufficient to fuse the ash. The black mass is cooled, treated with hydrogen peroxide (to prevent liberation of hydrogen sulphide), and boiled with 50 c c of  $\frac{N}{10}$  sulphuric acid. The filtrate and washings are titrated with  $\frac{N}{10}$  sodium hydroxide solution with methyl-orange or lacmoid (preferably the latter) as indicator. The liquid is then boiled with a few drops of  $\frac{N}{10}$  sulphuric acid to expel carbon dioxide, the acid neutralised with  $\frac{N}{10}$  alkali solution, and the titration with  $\frac{N}{10}$  sodium hydroxide solution completed after the addition of phenolphthalein.

To account for the remaining third of unneutralised phosphoric acid twice the number of c c of standard alkali used in the final titration are taken for the calculation.

The results obtained by this method, and by Hehner's method with vinegars containing known quantities of added sulphuric acid were as given in table on p 148

The difference between the two sets of results was attributed to the influence of the carbon dioxide on the methyl-orange, which caused the results to be too high.

By this method of Richardson and Bowen the amount of sulphuric acid originally added is shown, whereas Hehner's method gives that actually present in the vinegar at the time of analysis.

Sulphuric Acid Added	With Methyl Orange		With Lacmoid	
	Hehner's Method	Richardson and Bowen's Method	Hehner's Method	Richardson and Bowen's Method
Per cent	Per cent	Per cent	Per cent	Per cent
A, 0.098,	+ 0.033	+ 0.099	+ 0.0216	+ 0.099
B, 0.049,	- 0.033	+ 0.064	- 0.045	+ 0.045
C, nil,	- 0.080	+ 0.023	- 0.098	+ 0.004

**Combined Sulphuric Acid**—The proportion of sulphuric acid in the form of sulphates in vinegar varies considerably, as will be seen from the following analyses, made by the writer, of the vinegars of six of the leading manufacturers —

A, 0.03 per cent	D, 0.155 per cent
B, 0.10 „	E, 0.170 „
C, 0.032 „	F, 0.021 „

The vinegars B, D, and E were made by the inversion process, while the other three were mash-tun products

An attempt was made some years ago to condemn vinegars containing more than 0.03 per cent of combined sulphuric acid, and several prosecutions were initiated \*

Although the amount of combined sulphuric acid affords evidence that the vinegar was made by inversion of starch with sulphuric acid, it is not an infallible proof, for an amount of sulphate in excess of 0.03 per cent. might be also due to the use of a very hard water, or to sulphuring the casks, or washing them with a soluble

\* Dr Edmunds, Public Analyst for St James', writing in the *British Food Journ* (1900, p 21), stated that he regarded all vinegars containing more than 0.01 to 0.03 per cent of sulphates as adulterated

sulphite which had subsequently become oxidised to sulphate.

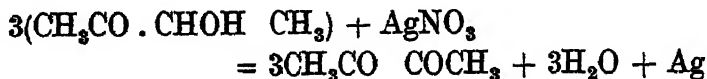
### OTHER CONSTITUENTS

**Detection of Methyl-Acetol.**—It has been shown by Pastureau \* that certain vinegars contain methyl-acetol,  $\text{CH}_3 \text{ CO CHOH CH}_3$ , probably derived from wood acid. It may be isolated by neutralising 100 c c of the sample with sodium hydroxide, and distilling the liquid to dryness.

If methyl-acetol is present, the distillate will reduce cold Fehling's solution, and when treated with iodine will give a precipitate of iodoform. When treated with phenyl-hydrazine acetate it will yield an osazone melting at  $243^\circ \text{C}$ , and giving a red coloration when dissolved in ether-alcohol and tested with ferric chloride, and red crystals on evaporating the liquid.

A quantitative estimation may be made by treating an aliquot part of the distillate with a few drops of sodium hydroxide solution and ammonia, and adding 10 c c. of  $\frac{N}{10}$  silver nitrate solution. The liquid is allowed to stand for 24 hours, diluted to 100 c c, and filtered, and the excess of silver titrated by the cyanide method.

From the amount of reduced silver the quantity of methyl-acetol is calculated by means of the equation—



One sample of vinegar thus examined contained 0.32 per cent of methyl-acetol. Or Kling's method † of estimation

\* *Journ Pharm Chim.*, 1905, [6], **xxi**, 593.

† *Bull Soc Chim*, 1906, **xxv**, 215.



with alkaline copper solution may be used, each gramme of methyl-acetol yielding 2.85 grammes of cuprous oxide

**Estimation of Formic Acid.**—Fincke\* has devised the following method of estimating formic acid in vinegar — Five c.c. of the sample are heated for two hours on the water bath beneath a reflux condenser with 5 grms of sodium acetate, 40 c.c. of a 5 per cent mercuric chloride solution and 30 c.c. of water, the liquid in the flask being completely immersed in the boiling water. The resulting precipitate of calomel is collected in a Gooch's crucible, washed with water, alcohol and ether, and dried and weighed. The weight multiplied by the factor 0.0977 gives the amount of formic acid.

The method affords an indication of the presence of added acetic acid in some vinegars, since commercial acetic acid almost invariably contains formic acid as an impurity. It is essential, however, that no caramelised sugar should be present, for sugar yields appreciable quantities of formic acid when heated to 160° C, at which temperature caramelisation begins.

Hence, as caramel is universally employed for colouring fermentation vinegars in this country, no reliance can be placed upon the results of the formic acid test if applied to coloured vinegars.

Moreover, although formic acid does not appear to be produced in the manufacture of spirit vinegar, it is found as a normal constituent in wine vinegars,† and probably also in other kinds of vinegar to which no caramel has been added.

\* *J Soc Chem Ind*, 1911, xxx, 82, 235, 916

† *Analyst*, 1911, xxxvi, 496

**Determination of Total Nitrogen.**—The nitrogenous substances in malt are readily transformed into ammonium sulphate by Kjeldahl's process, and a clear solution may be obtained in about an hour by adding a little potassium bisulphate to the sulphuric acid. The addition of mercury accelerates the process, but, as a rule, is not necessary. From 10 to 25 c c of the vinegar are used for the determination.

**Nature of Nitrogenous Substances.**—Only a small proportion of the nitrogen in vinegar appears to be in the form of ammonium salts or albumoses precipitable by ammonium or zinc sulphates. In one experiment in which 1 000 c c of vinegar brewed from barley malt were concentrated to 100 c c, and aliquot portions used for the different estimations, the following results were obtained by the writer —

	Per cent
Total nitrogen	0 1204
Nitrogen in precipitate given by ammonium sulphate (after evapo- ration with water and barium carbonate),	(1) 0 0127 (2) 0 0157
Nitrogen in zinc sulphate precipitate,	0 0148
Ammoniacal nitrogen,	0 015

Similar results were obtained with a sample of commercial malt vinegar —

	Per cent
Total nitrogen,	0 089
Nitrogen precipitated by ammonium sulphate,	0-008
Ammoniacal nitrogen,	0-007

**Determination of Phosphoric Acid.**—Of the many processes devised for determining small quantities of phosphoric acid one of the most simple and accurate for the analysis of vinegar is the modification of the molybdate method devised by Hehner

The ash from 10 c c of the sample is dissolved in the smallest possible quantity of dilute nitric acid, and treated with a large excess of an ammonium molybdate solution. The basin is allowed to stand for 12 hours at the ordinary temperature, or for two hours on the top of a hot-water oven, after which the yellow precipitate is washed twice by decantation with cold water. It is then dissolved in ammonia solution, the liquid evaporated, and the residue dried on the water bath. The weight divided by the factor 28.5 gives the amount of phosphoric acid ( $P_2O_5$ )

The molybdate reagent may be prepared by dissolving 50 grms of molybdic acid in a mixture of 50 c c of ammonia solution and 150 c c of water. When cold, the solution is cautiously added to a cold mixture of 280 c c. of nitric acid and 470 c c of water, and the reagent is filtered after standing for some hours.

As a rule, the amount of phosphoric acid in a vinegar brewed from malted or unmalted barley will exceed 0.05 per cent, but the amount may be increased by the use of yeast foods to aid the fermentation, or may be reduced by clarification processes in which the wort is fined by the addition of soluble calcium salts.

**Reducing Sugars.**—The following method of estimating the reducing sugars in cider vinegar is recommended by Leach and Lythgoe\* —Two portions (25 c c each)

\* *J Amer Chem Soc*, 1904, xxvi, 375

are taken One is diluted with 20 c c of water and heated with 5 c c of hydrochloric acid for ten minutes, and then cooled Both portions are neutralised with sodium hydroxide and made up to 100 c c, and tested with Fehling's solution The amount of reducing sugars ought to be the same before and after inversion, any increase denoting the presence of cane sugar

The ratio between the weights of total solids and dextrose affords a means of detecting glucose vinegars in wine vinegars (see p 187)

**Detection of Inositol in Wine Vinegar.**—It has been shown by Meillère\* that inositol is a constituent of all wines, and since this sugar is not decomposed during acetic fermentation, its separation and identification affords a means of distinguishing between wine vinegar and spirit vinegar

The following method of applying the test was devised by Fleury† —One hundred c c of the vinegar are evaporated nearly to dryness, and the residue taken up with 50 c c of water, neutralised with sodium hydroxide, and ground up with 3 grms of barium hydroxide The precipitate is separated, with the aid of centrifugal force, and washed with 20 to 30 c c. of baryta water, and the filtrate and washings freed from barium by means of a current of carbon dioxide, after which 10 c c of dilute lead acetate solution are added, and the new precipitate separated as before The filtrate is concentrated to 100 c c., and treated with 10 c c of the official basic lead acetate solution (lead acetate, 300 grms, lead oxide, 100 grms., water, 700 c c, shaken and filtered), and

\* *Journ Pharm Chim*, 1908, [8], xxviii., 289.

† *Ibid*, 1910, [7], ii., 264.

2 grms of neutral cadmium acetate in solution The precipitate containing the inositol is washed and decomposed with hydrogen sulphide, and filtrate from the cadmium sulphide is concentrated to a syrup, and treated with 20 c c of absolute alcohol and 5 c c of anhydrous ether, and allowed to stand for 24 hours The crystals of inositol which form in the case of a wine vinegar are separated and identified

Tests of identity have been based upon the oxidation of the sugar into a quinonic compound, rhodizonic acid, some of the salts of which are of a bright red colour

Seidel dissolves a little of the precipitate in water, and treats the solution with a drop of Millon's reagent \* The liquid is evaporated to dryness, the residue dried at 110° to 120° C, and treated with 3 c c of glacial acetic acid, and one drop of a 10 per cent solution of strontium acetate, and the solution evaporated on the water bath A bright red coloration and deposit are obtained

Another proof of identity is to evaporate the residue with Gallois' mercuric reagent, which is prepared by dissolving 1 gm of yellow mercury oxide in a mixture of 1 c c of nitric acid and 10 c c of water, and diluting the solution to 20 c c The resulting mercury rhodizonate is a brilliant red salt

**Detection of Malic Acid.**—Cider vinegar should always contain malic acid, and the following tests for its detection are recommended by Leach and Lythgoe †  
—The vinegar should give a precipitate with lead acetate,

\* One part of mercury is dissolved in 2 parts of nitric acid (40° B), and the solution diluted with an equal volume of water, and after 24 hours decanted from the crystalline deposit

† *J Amer Chem Soc*, 1904, xxvi, 375

subsiding rapidly. The presence of malic acid is then confirmed by treating 5 c c of the vinegar with 1 c c of 10 per cent calcium chloride solution filtering, and adding 3 volumes of 95 per cent alcohol to the filtrate. A flocculent precipitate will be obtained if malic acid be present.

The addition of the alcohol will also precipitate dextrin, but this may be detected by a dextro-rotatory reading in the polarimetric test.

A precipitate should also be obtained with calcium sulphate after drying the calcium chloride precipitate, dissolving it in nitric acid, and evaporating the solution on the water bath to convert the calcium malate into calcium oxalate, which is then decomposed by boiling with sodium carbonate. The filtrate from the calcium carbonate is then acidified with acetic acid, and tested with calcium sulphate solution.

**Tartaric Acid.**—If the total solids left on evaporation of wine vinegar be treated with absolute alcohol, a granular residue of hydrogen potassium tartrate will be left undissolved. The nature of this deposit may be confirmed by dissolving it in the smallest possible quantity of hot water, and stirring the solution in a watch-glass by means of a glass rod. The cream of tartar will then be re-deposited in streaks following the lines of the rod.

The following confirmatory test of identification, devised by Denigès, may also be applied.—The crystals are added to a reagent consisting of 3 c c of sulphuric acid and 3 drops of a solution of resorcinol (2 grms in 100 c c of water acidulated with 5 c c of sulphuric acid), and the mixture heated to 130° to 140° C. In the presence of tartaric acid an intense carmine-red coloration is produced.

For the estimation of the potassium bitartrate 25 c c of the vinegar are evaporated to a syrup. This is dissolved in 25 c c of water, and the solution mixed with 100 c c of alcohol-ether (1 : 1), and allowed to stand for 24 hours in a cool place. The resulting precipitate is washed with alcohol-ether, and dissolved in hot water, and the solution titrated with  $\frac{N}{10}$  alkali. Each c c required corresponds to 0.0188 gm of potassium bitartrate.

**Citric Acid.**—This may be detected by the test devised by Denigès for wines.—Ten c c of the vinegar are shaken with 1 gm of lead peroxide and 2 c c of mercuric sulphate solution, and filtered. About 5 c c of the filtrate are boiled and treated with a drop of a 1 per cent solution of potassium permanganate solution, after decolorisation an additional 10 drops are added, one by one. Normal wine vinegars yield a slight turbidity in this case, while those containing 0.10 gm or more of citric acid per litre give a pronounced turbidity.

**Oxalic Acid.**—The following method is recommended by Calvet \*—Fifty c c of the vinegar are neutralised, and the oxalic acid precipitated as calcium oxalate by means of calcium acetate. The precipitate is washed and oxidised with a standardised sulphuric acid solution of potassium permanganate, or it is sulphated, dried, and weighed as calcium sulphate. The weight multiplied by the factor 1.855 gives the amount of oxalic acid per litre of vinegar.

## COLOURING MATTERS

The recommendation of the Local Government Board, to the effect that the only colouring matter which it

\* *Alcool Méthylique, Vinaigres*, 1912, p. 136

should be permissible to add to vinegar should be caramel is almost universally accepted in this country

Vinegar brewed from malt or malt and cereals is of too pale a colour to be generally acceptable, except in Scotland and it is, therefore, essential to add some colouring matter to meet the popular taste. Although aniline dyestuffs may possibly be used for this purpose, caramel has long been regarded as the most suitable colouring matter from every point of view

**Measurement of Colour Intensity.**—Owing to the great variations in the tinctorial power of different varieties of caramel, it is not easy to fix upon a standard substance upon which to base subsequent measurements. Even if a standard solution is made up from a particular sample of caramel and kept for comparison with subsequent samples, gradual fading takes place, especially if the bottle is exposed to the light. Some slight decomposition and deposition of the pigment is also inevitable in the course of time

An iron compound which, when dissolved, would give the required shade of colour might possibly be used for the purpose, but this would involve the use of an absolutely pure salt, which would have to be weighed out and dissolved before each comparison, since it would not be stable in solution

Iodine solutions of standard strength were adopted by the Berlin Congress of 1903 for measuring the colour of malt products, but they are only suitable for light-coloured worts, since the tint of iodine is considerably redder than that of strong malt worts

To obviate this drawback Brand and Jais\* suggested

\* *Zeit ges Brauw*, 1906, **xxix**, 337



the use of aniline dyestuffs to obtain a standard corresponding in intensity of shade to  $\frac{N}{10}$  iodine, and equivalent in colour tone to the colouring matter of malt or caramel at all concentrations

This system has the same drawbacks as the use of an iron salt, especially the deterioration of the tinctorial value of the standard solutions on keeping

Hence, the invention of Lovibond's tintometer has been of material service to all who have to match and keep a record of colours, and the apparatus is now extensively used in many industries

**Lovibond's Tintometer.**—The use of this instrument is based upon a comparison of the coloured substance with a series of standard coloured glasses, which can be blended in such a way as to give the same colour sensation

For the purposes of brewers and vinegar makers a special series of these glasses approximating to the colour of solutions of malt extract or caramel is provided, the liquid being placed in a glass cell 1 inch or  $\frac{1}{2}$  inch in width, while the numbered glasses are placed in a small holder, and viewed simultaneously through the instrument in a good light

It has been shown by Baker and Hulton \* that agreement between the results obtained by different observers depends on various conditions, such as the relation of the instrument to the source of light, and from the results of their experiments they make the following recommendations —(1) The tintometer should be used in a horizontal position directed to a north window covered with white tissue paper, (2) it should not be more than

\* *Journ. Inst. Brewing*, 1907, xiii, 26

2 to 3 feet from the window. and (3) the opal screen of the instrument should be discarded

In the writer's experience it is possible to match the colours of most vinegars by means of the '52' series of glasses, although in some cases a glass of the "50" series may be required.

When examined in a 1-inch cell the pale vinegars of commerce range from about 5 to 10 in the "52" series, medium-coloured vinegars from 15 to 20, and dark vinegars from 30 to 40

In the case of the darkest products it is advisable to

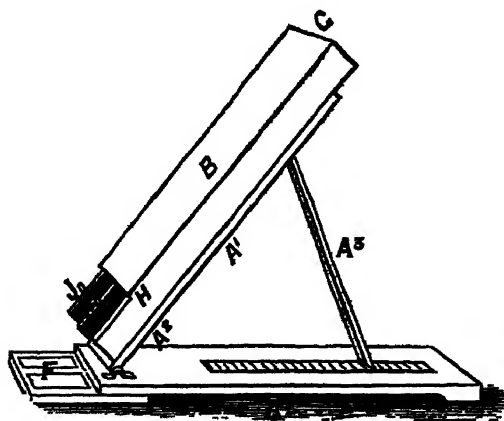


Fig. 52 —Lovibond's Tintometer

dilute the liquid with an equal volume of water, since the results of two observers will agree better under such conditions than when a very dark liquid is examined without dilution.

## DETECTION OF CARAMEL

**The Fuller's Earth Test.**—It is frequently possible to precipitate the whole of the added caramel by treating the vinegar with a little fuller's earth that has been

proved to be active in this respect For example, wood vinegar may usually be completely decolorised in this way

But when applied to vinegars which owe part of their colour to products formed in the drying of the malt or gram too much reliance must not be placed upon this test

Thus, it has been shown by Dubois \* that the amount of colour removed from a cider vinegar may vary from nothing to 72 per cent, and that the proportion will differ with different kinds of earth Hence, a sample of vinegar which gave no deposit when treated with one earth, would be regarded as containing added caramel when treated with another earth Nor are the results given by the same earth uniform Thus, in Dubois' experiments, an earth which removed no colour from one pure vinegar removed the larger proportion from another pure sample.

At best, the test must be regarded as a preliminary one. If all colour is removed, caramel is undoubtedly present, while if little or no colour is removed the sample may be regarded as free from caramel But in the case of most vinegars, from which about 25 to 75 per cent of colour is removed, the test is inconclusive

Lichthardt † uses a method of precipitation with tannin as a test for caramel in vinegar, flavouring extracts, etc. Five c.c of a solution of 1 grm of gallotannic acid and 0.75 grm. of sulphuric acid (sp. gr. 1.84) in 50 c.c of water are added to the vinegar, and the mixture heated until the precipitate that first forms is dissolved The

\* *J. Amer. Chem. Soc.*, 1907, **xxix**, 75

† *J. Ind. Eng. Chem.*, 1910, **ii**, 389

liquid is then allowed to stand for 12 hours, and in the presence of caramel a light or dark brown deposit will be present.

The objection to this test is that albuminous substances and iron compounds also react with tannin, so that the formation of a precipitate is not a conclusive indication of caramel

The method officially used in France for wine vinegar is to shake 50 to 100 c c of the sample with 50 c c of ether, to allow the colourless ethereal layer to evaporate spontaneously, and to test the residue with 2 to 3 drops of freshly prepared 1 per cent solution of resorcinol in hydrochloric acid. In the presence of caramel a rose coloration will be obtained (Fiehe's reaction)

If the ethereal layer is coloured, it should be washed with water rendered slightly ammoniacal, and evaporated. Or, if necessary, the residue may be taken up with 25 c.c of water, and the solution boiled with a little egg-albumin (white of egg), the colouring matter being removed by the coagulated albumin

It has been shown by Anderson\* that pure cider vinegars contain furfural, and that Fiehe's reaction is, therefore, not necessarily an indication of the presence of caramel in such vinegars

Amthor† bases a method of detecting caramel upon its precipitation with paraldehyde. Ten c c of the vinegar are mixed with 30 c c of paraldehyde and sufficient absolute alcohol to obtain a clear solution, and the mixture left for 24 hours in a closed flask.

The precipitate is washed with absolute alcohol and dissolved in water, and the solution evaporated to 1 c.c.,

\* *Ibid*, 1914, vi., 214.

† *Zeit anal. Chem*, xxiv, 30

and heated for 30 minutes at 100° C with a small quantity of an acetic acid solution of phenyl-hydrazine. If the precipitate consisted of caramel an amorphous compound (probably composed of phenyl-hydrazones and osazones) is obtained.

Various colorimetric methods of estimating caramel have been suggested (*e g*, by Smith, *Amer J. Pharm*, 1911, lxxxiii., 411), but since commercial samples vary widely in their chemical composition, according to the different methods of manufacture in use, none of these can lay claim to much accuracy

In practice caramel is bought upon the basis of its colouring capacity without reference to the chemical compounds to which its colour is due

The method recommended by a Committee of the Institute of Brewing\* is essentially the same as that used by the present writer for many years.—Ten grms. of the sample are dissolved in 100 c c of water at 15·5° C., and the solution diluted to a litre, and compared in a 1-inch cell with glass of "52" series in Lovibond's tintometer

**Coloured Wine Vinegars.**—The coloration of wine vinegars with cochineal or archil is allowed by the French law The official methods used in France in the detection of these colouring matters are as follows :—

**Cochineal.**—Twenty-five c c. of the vinegar are shaken for five minutes with 20 c c. of ether, and the ethereal extract treated with a few drops of ammonia solution. In the presence of cochineal a carmine red coloration is obtained

As a confirmatory test 4 c.c. of the vinegar are neutralised and treated with 1 c c of a 1 per cent. solution of

\* *Journ. Inst Brewing*, 1910, xvi, 529.

ammonium alum followed by 1 c. c. of a 10 per cent sodium carbonate solution. The resulting lake will be bluish-violet, and the filtrate violet, if the colouring matter was cochineal.

**Archil.**—Twenty-five c. c. of the vinegar are made slightly alkaline with ammonia, and shaken with 10 c. c. of amyl alcohol, a violet coloration being obtained in the presence of archil. The extract is evaporated, and the residue treated with one drop of sulphuric acid, which gives a coloration changing to bluish-violet on addition of ammonia.

## METALLIC IMPURITIES

Vinegar is very liable to become contaminated with metallic impurities, such as iron and copper, derived from hoops upon the vats, brass taps, and the like, with which it may come into contact.

**Iron.**—The presence of traces of iron is mainly of importance from the fact that when the vinegar comes in contact with the wood in a new barrel a black iron tannate will be formed, which will cause the vinegar to become dark and unsaleable.

The presence of iron may be detected by adding potassium ferrocyanide directly to the vinegar, and it may be estimated colorimetrically in the ash by means of the same reaction.

**Copper, Lead, and Tin.**—For the detection of these metals 100 c. c. of the vinegar are boiled with 10 c. c. of hydrochloric acid, and potassium chlorate introduced in small quantities at a time until a colourless solution is obtained. This is treated with sodium acetate to remove

the hydrochloric acid and a current of hydrogen sulphides passed through the liquid

Copper may be estimated electrolytically in the vinegar itself. A few drops of nitric acid are added to 100 c.c. of the sample, which is then electrolysed for 30 minutes with a current of 2 volts and 1 amp. per square decimetre. The copper is deposited on the electrodes in the usual way.

In testing for lead the ash from the vinegar is moistened with acetic acid and treated with an excess of dilute ammonia solution, and the liquid boiled and filtered. This treatment is repeated several times to effect complete extraction, and the filtrates are united, and made up to a definite volume. In the presence of copper a brown coloration will be obtained on the addition of potassium ferrocyanide to a small part of the liquid.

If no copper is found, the solution is rendered acid with hydrochloric acid, and tested for lead with a solution of hydrogen sulphide.

When copper is present an addition of a small quantity of potassium cyanide should be made before applying the test for lead. The ferrocyanide test for copper and the hydrogen sulphide test for lead may be used for the colorimetric estimation of traces of those metals, the tint produced being matched with standard solutions of lead and copper salts.

**Tin.**—The ash of the vinegar is fused with sodium hydroxide, and the mass extracted with boiling water containing a little hydrochloric acid. The filtered extract is tested with hydrogen sulphide, which in the presence of tin gives a yellow coloration or precipitate.

**Arsenic.**—The discovery, in 1900, that several cases of

peripheral neuritis had been caused by drinking beer containing arsenic drew general attention to the possibility of the occurrence of dangerous amounts of arsenic in other food products

The Royal Commission appointed in 1901 to investigate the subject found that the glucose used in the preparation of these arsenical beers contained quantities of arsenic ranging from 0.015 to 0.131 per cent., and that in the case of one sample of beer the amount of arsenic reached 3 grains per gallon

The original source of this arsenic was discovered in the sulphuric acid used in the preparation of the brewing sugar, some of the samples of acid containing as much as 2.5 per cent. of arsenic (as arsenious acid).

Arsenic was also detected in other beers brewed from malt, the poison being ultimately traced to the fuel used for the kilns.

Since vinegars are brewed upon similar lines to beer, it is not surprising that traces of arsenic were found in many samples, and that serious, if not dangerous, quantities were present in vinegars made by the conversion process, where impure sulphuric acid had been employed.

Another possible source of arsenic in vinegar is the caramel, which is almost universally employed as a colouring material. This is often prepared from glucose, and the use of impure acid in the hydrolysis of the starch has been known to cause arsenic to be present in the caramel.

After the publication of the report of the Royal Commission in 1903 precautions were taken by the maltsters and the manufacturers of brewing sugars to prevent recurrence of the trouble, and, as a rule, the malt now



upon the market seldom contains over  $\frac{1}{250}$  grain of arsenic per pound

In 1901 a Conjoint Committee of the Society of Chemical Industry and of the Society of Public Analysts was appointed to examine and report upon the various methods of detecting and estimating arsenic, and in the following year issued the subjoined report,\* which, if exactly followed, will give accurate results under all conditions —†

**“MATERIALS REQUIRED—Hydrochloric Acid**—The purest hydrochloric acid obtainable is very rarely free from arsenic To the ‘pure’ acid, as purchased for analysis, diluted with distilled water to a specific gravity of 1.10, sufficient bromine is added to colour it strongly yellow (about 5 c.c. per litre), sulphurous acid, either gaseous or in aqueous solution, is then added in excess, and the mixture is allowed to stand for at least twelve hours, or hydrobromic and sulphurous acid may be used The acid is then boiled till about one fifth has evaporated, and the residue can either be used directly or may be distilled, the whole of the arsenic having volatilised with the first portion

**“Sulphuric Acid**—This is more frequently obtainable arsenic-free than hydrochloric acid If not procurable, to about half a litre of sulphuric acid ‘pure for analysis,’ a few grammes of sodium chloride are added, and the mixture distilled from a non-tubulated glass retort, the first portion of about 50 c.c. being rejected For the purpose of the test to be described, one volume of the distilled acid is diluted with four volumes of water.

**“Nitric acid** can, as a rule, be obtained free from arsenic without much difficulty the pure redistilled acid should be used This should be tested by evaporating 20 c.c. in a porcelain dish, which should then be washed out with dilute acid, and tested as described in this report

**“The purified acids** should be prepared as required, and should not be stored for any length of time If this is unavoidable, however, Jena flasks are to be preferred, since most bottle glass is liable to communicate traces of arsenic

**“Zinc.**—Arsenic free zinc is obtainable from chemical dealers It should be regranulated by melting it and pouring it from some height into cold water

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\* The report is condensed here, the directions for testing beer are also applicable to vinegar

† *Analyst*, 1902, xxvii., 48

"**Lime**—Caustic lime, even when made from white marble, is not always free from arsenic. A selection must, therefore, be made from various samples. If pure lime is not obtainable, magnesia may equally well be used, and can be more readily obtained of sufficient purity.

"**Calcium Chloride**.—This salt often contains arsenic, and before being used as a drying agent must be freed from the volatilisable part of the impurity by moistening it with strong hydrochloric acid, fusing and re-granulating.

"**Apparatus**.—A bottle or flask holding about 200 c c (for frothing materials preferably wider at top than bottom) is fitted with a double-

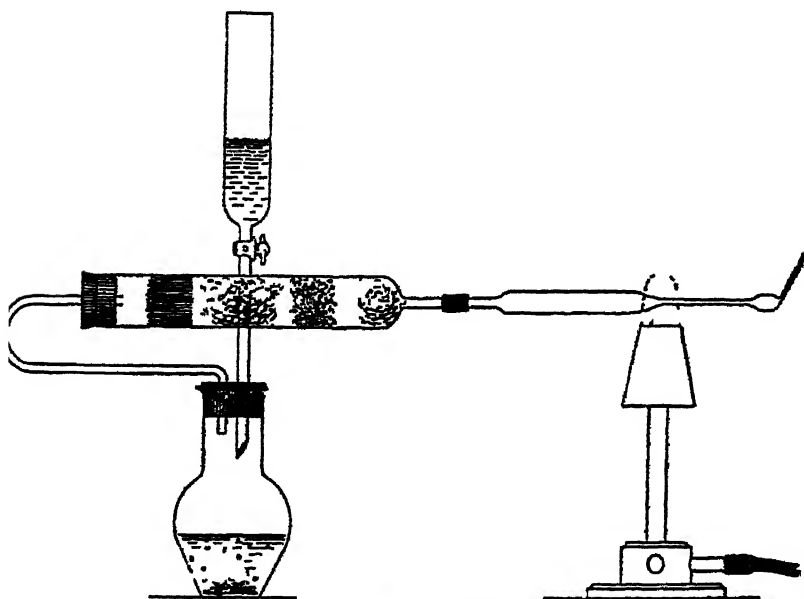


Fig. 53—Arsenic Apparatus

bored cork, india-rubber stopper, or with a ground-in glass connection, carrying a topped funnel (holding about 50 c c), and an exit tube. The latter is connected with a drying tube containing, first, a roll of blotting paper soaked in lead acetate solution, and dried, or a layer of cotton wool prepared in a similar way, then a wad of cotton wool, then a layer of granulated calcium chloride, and finally a thick wad of cotton wool. To this tube is fitted a hard-glass tube drawn out as shown in the figure, and of such external diameter that at the place where the arsenic mirror is to be expected the tube just passes through a No 13 Birmingham wire gauge (corresponding with 0.092 inch). The exact size is not material, but all

tubes used for standards and tests should be as nearly as practicable of the same diameter. A good Bunsen flame is used to heat the hard-glass tube close to the constriction. About 1 inch of tube, including the shoulder, ought to be red hot. A piece of moderately fine copper gauze (about 1 inch square) wrapped round the portion of tube to be heated assists in insuring equal distribution of heat. A suitable form of apparatus is shown in the accompanying figure.

About 20 grammes of zinc are placed in the bottle and washed with water to clean the surface, as particles of dust may contain arsenic, all parts of the apparatus are connected, and a sufficient quantity of acid (prepared as previously described) allowed to flow from the funnel, so as to cause a fairly brisk evolution of hydrogen. When the hydrogen flame, which during the heating of the tube should be kept at as uniform a height as possible (about a quarter of an inch), burns with a round, not pointed, tip, all air has been removed from the apparatus. The Bunsen burner should then be placed under the hard glass tube as described, and more acid (10 to 20 c.c. are generally enough) run in as required. With good materials no trace of a mirror is obtained within half an-hour.

"Great care must be taken that when additions of acid are made to the zinc no bubble of air is introduced, since in presence of air the arsenic mirror may become black and unevenly distributed, whilst it is brown when the experiment has been properly conducted.

"Should the blank experiment not be satisfactory, it must be ascertained by changing the materials methodically whether the fault lies with the acid, zinc, other materials, or with the apparatus.

"**Preparation of Standard Mirrors.**—When a satisfactory blank experiment has been obtained a series of standard mirrors must be prepared under the following conditions.—A hydrochloric acid solution of arsenious oxide containing in each c.c. 0.001 milligramme  $\text{As}_2\text{O}_3$  is prepared by diluting a stronger solution with distilled water. Two c.c. of this solution (equal to 0.002 milligramme of arsenious oxide) are introduced into the apparatus, a new tube having been joined to the drying tube. If the zinc is sensitive a distinct brown mirror is obtained after twenty minutes. It is important to note that some 'pure' zinc is from a cause at present unknown\* not sufficiently sensitive—that is to say, the addition of minute quantities of arsenic produces no mirrors. The portion of tube containing the mirror should be sealed off while still filled with hydrogen, in contact with air the mirrors gradually fade. Mirrors are now similarly made with 0.004, 0.006, 0.008, and 0.01 milligramme of arsenious oxide. With a little

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\* Chapman and Law, *Analyst*, 1906, 3

patience it is easy to obtain the deposits of arsenic neatly and equally distributed. The standard mirrors, properly marked, are mounted on a white card or porcelain slip. It is to be understood that the first stage of every test must be a blank of at least twenty minutes.

"Organic materials, such as yeast, beer, etc., cannot be tested when sulphuric acid is used, without destruction of organic matter, whilst as a rule they can be directly tested with hydrochloric acid.

"**Procedure without Destruction of Organic Matter.**—The apparatus is started, and a blank experiment allowed to go on for 20 minutes. If no trace of deposit is obtained 10 c.c. of the liquid to be tested and about 10 c.c. of hydrochloric acid are put into the funnel and slowly introduced into the bottle without air-bubbles. Some materials (beers, for example) are apt to froth, hence the necessity for slow introduction. If after about 10 minutes no mirror appears, another 10 c.c. of the liquid, with 10 c.c. of hydrochloric acid, are added, and the experiment continued for 15 to 20 minutes, acid being added from time to time as may appear necessary.

"**Malt.**—Fifty grammes of the malt are placed in a 300 c.c. separator funnel with a stopcock, 50 c.c. of hydrochloric acid, prepared as described, and 50 c.c. of water are warmed to about 50° C. and poured on the malt. The whole is then allowed to digest for 15 to 20 minutes with frequent agitation, and the acid then allowed to run off by the stopcock. About 60 c.c. of the acid liquor is thus obtained, of which 20 c.c. contains the arsenic from 10 grammes of malt.

"Sugar and other brewing materials are dissolved in water, 10 c.c. of acid added, and the solution tested direct, operating upon 10 to 20 grammes of material.

"**Destruction of Organic Matter—(a) Acid Method.**—Ten grammes of the substance are placed in a 3½-inch porcelain crucible, and covered with pure distilled nitric acid (about 10 to 15 c.c.). The whole is then heated on a sand bath until the evolution of brown fumes ceases. Three c.c. of concentrated arsenic-free sulphuric acid are then added, and the heating continued until the mass just begins to char, when a further quantity of 5 c.c. of nitric acid is added. The heating is now continued until all acid is expelled, leaving in the crucible a black, nearly dry, charred mass. The crucible is about half filled with water, and a few c.c. of hydrochloric acid or dilute sulphuric acid run in (according as the one or the other is to be used in the Marsh apparatus), the whole being allowed to extract for about half-an-hour on a water-bath. It is then filtered into a porcelain basin, the charred mass washed with hot water, and the filtrate concentrated down to about 30 c.c., which is allowed to cool, and is then ready for the

test. It is essential that the mass should be thoroughly charred, and that the solution when filtered should be colourless.

"In the case of beer, 10 to 20 c c are evaporated to dryness, and the residue oxidised as above stated.

"(b) *Basic Method*—The materials are mixed with pure lime or magnesia (1 gramme for 20 c c of beer), dried, and incinerated. For sugars or other solid materials about half their weight of base is employed. The ash is dissolved in hydrochloric acid and the solution tested.

"The proof that the mirrors are arsenical is obtained as follows—The narrow portion of the tube containing the mirror (which should not be denser than that produced by 0.01 milligramme of arsenious oxide) is cut off, the hydrogen replaced by air, and the ends sealed up. The tube, held in the tongs, is then heated by drawing it repeatedly through the flame of a Bunsen lamp until the mirror has disappeared. On cooling, minute crystals of arsenious oxide deposit, the sparkling of which can be seen by the naked eye if the tube be held before a luminous flame, and which can be readily identified under the microscope by their crystalline form.

"This test, as recommended, is one of such extreme delicacy that with quantities of 20 grammes (or 20 c c) it will give an indication of the presence of 0.000015 per cent (or 1 part in 7,000,000) of arsenious oxide."

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## CHAPTER X.

## CHARACTERISTICS OF DIFFERENT VINEGARS.

Interpretation of Results—CHEMICAL STANDARDS—Acetic Strength—Total Solids—"Original Solids"—Nitrogen and Phosphoric Acid—Optical Standard—MALT VINEGARS—The Malt Vinegar Question—Composition of Malt Vinegars—Cider Vinegar—Wine Vinegar—Whey Vinegar—Fruit and Herb Vinegars—Date Vinegar—Spirit Vinegars—Essig-sprit—Wood Vinegar—Composition of Artificial Vinegars

THE interpretation of the results of an analysis is by no means an easy problem in the case of certain kinds of vinegar. Although analysis will show that a vinegar must be a wood vinegar or spirit vinegar or distilled vinegar, it is not possible to state with certainty the origin of some grain vinegars. For example, a safe deduction may be drawn from the deficiency of certain constituents that a vinegar has not been manufactured in a normal way from malted or unmalted barley, but it may not be justifiable to assert that it has not been derived from a mixture of malted barley and unmalted cereals. In the absence of legal standards for the composition of the different kinds of vinegar, the analyst can only draw probable conclusions from a comparison of his figures with the average results of products presumably brewed in the same way. The danger of placing too much reliance upon such comparisons was shown in a recent prosecution for the sale of a vinegar which the analyst asserted was not wholly derived from malt. The Stipendiary, in dis-

missing the case, remarked, ' This is not an analysis, but a guess "

## CHEMICAL STANDARDS FOR VINEGAR

**Acetic Strength.**—The standard suggested by the Local Government Board in their definitions of vinegar and artificial vinegar, of a minimum of 4 per cent of acetic acid, has already been mentioned

There have been numerous prosecutions and convictions for the sale of vinegar containing less than 4 per cent of acetic acid, and the bulk of the vinegar sold throughout the country is now in excess of the 4 per cent. standard

There is, however, no general agreement on the point, and even during the current year conflicting decisions have been given by magistrates.

Legal standards for the strength of vinegar are found in the food regulations of some of the Colonies and in foreign countries For example, in Australia and in the United States the same minimum standard for strength (4 per cent.) has been adopted

**Standard for Total Solids.**—Early in 1907 the London and Country Vinegar Brewers' Association passed a resolution, to the effect that the conditions specified in the Admiralty contract were a correct definition of what No 20 Vinegar should be —

" The vinegar of No 20 trade denomination, which contains 5 17 per cent or 22 6 grains by weight of real acetic acid ( $C_2H_4O_2$ ) per fluid ounce It shall have a specific gravity at 60° F. of 1 017 to 1 021, and be wholly the product of alcoholic, acetous fermentation in the

vinegar itself, and that they were prepared to support local authorities in establishing such a standard, and that higher and lower strengths of vinegar be based on this definition \*

No attempt was made by the Local Government Board to give force to this proposed standard of a minimum of total solid matters. In fact, one firm declined to support the resolution upon the ground that to leave a large proportion of unfermented substances in the wash would lead to bad and uneconomical brewing.

Moreover, a well-attenuated wash from an all-malt brew might have a much lower specific gravity than a wash prepared from glucose containing a large amount of unfermentable substances. At best, such a standard would have had the effect of making a sharper differentiation between brewed and artificial vinegars, which are usually sold at a cost that would not permit of the addition of suitable substances to raise the specific gravity.

**Calculation of "Original Solids."**—An empirical but convenient method of comparing the analytical results of the examination of vinegars of different acetic strength was devised by *Hehner* †

It is based upon a calculation of the percentage of the different constituents upon 100 parts of the solid matter estimated to have been present in the original wort. Since 180 parts of dextrose can be theoretically converted into 120 parts of acetic acid, the "original solids" are found by multiplying the percentage of acetic acid by the factor 1.5 and adding the product to the amount of total solids still remaining in the vinegar.

For example, in the case of a vinegar containing 4.92

\* *Dr. Hamill's Report*, 1908, p. 16.

† *Analyst*, 1891, xvi, 92



per cent of acetic acid and 2.27 per cent of total solids, the "original solids" would be  $(4.92 \times 1.5) + 2.27 = 9.65$  per cent

It was pointed out by Allen and Moore\* that in practice the yield of acetic acid seldom exceeds two-thirds of the theoretical amount, so that a more correct estimation of the original solids in the wort would be made by multiplying the amount of acetic acid by  $\frac{3}{2}$  (= 2.25) and adding this result to the total solids found in the vinegar. Applying this method of calculation to the example given above, the "original solids" would be 13.44 per cent.

As it is impossible, owing to the variety of materials used for brewing, and the variations in the loss on acetification, to arrive at a true figure for the "original solids," there seems to be no advantage in substituting the value as calculated by Allen and Moore for the theoretical value suggested by Hehner.

**Nitrogen and Phosphoric Acid.**—The proportion of one or both of these constituents calculated upon the "original solids" of the vinegar is usually taken into consideration in giving an opinion upon the origin of a vinegar.

In the case of a vinegar brewed from an average barley malt, the amounts of nitrogen and phosphoric acids in the "original solids" will usually exceed 0.5 per cent, and the two quantities of the two constituents will be approximately equal. This is, of course, assuming that no process has been used whereby the proportion of either is reduced.

Barley malts vary widely in their composition, as is shown by the following analyses by Salamon† of sixteen samples of dried malt—

\* *Ibid*, 1893, xviii, 245.

† *J. Soc. Chem. Ind.*, 1885.

	Mineral Ash	Total Nitrogen from Nitrogenous Substances	Total Nitrogen from Soluble Nitrogenous Substances	Phosphoric Anhydride, P <sub>2</sub> O <sub>5</sub>
Highest,	Per cent 3.41	Per cent 1.70	Per cent 1.193	Per cent. 1.10
Lowest,	2.09	1.27	0.662	0.635

It will thus be seen that malt made from badly-germinated barley will contain much less soluble nitrogen than that from well-grown barley that has germinated satisfactorily.

At the same time, it is hardly probable that vinegar made from a malt containing only relatively small amounts of soluble nitrogen and phosphoric acid, such as the lowest figures recorded above, would contain less than the 0.5 per cent of each constituent calculated upon the original "solids."

But the conditions are totally different when a mixture of malted barley or other malt with raw grain is used, as is obvious from a glance at the following analyses made by Gilbert —\*

	Barley	Rye	Mauze	Oats
	Per cent	Per cent	Per cent	Per cent
Moisture,	12.0	14.3	11.5	14.2
Starch,	52.7	54.9	54.8	56.1
Gums and sugars,	4.2	11.3	2.9	5.7
Albuminoids (soluble and insoluble),	13.2	8.8	8.9	16.0
Cellulose,	11.5	6.4	14.9	1.0
Fat,	2.6	2.0	4.7	4.6
Ash,	2.8	1.8	1.6	2.2
Total.	99.0	99.5	99.3	99.8

\* Quoted by Nettleton, *The Manufacture of Spirit*, p. 392.

Again, according to von Bibra,\* the ash of rye ranges from 1.97 to 2.05, and the proportion of phosphoric acid therein from 42.38 to 50.35

Hence, vinegars brewed from mixtures of a malted grain with any of these raw grains would show enormous variations in the proportions of nitrogen and phosphoric acid. If rye were used the values for both the constituents would be very much lower than if barley were the grain, while if rice were the cereal employed the percentages would be still less, and would fall far below those of a vinegar brewed from an average malted barley or a mixture of malt and barley.

For these reasons it is obvious that even if the definition of malt vinegar as a cereal product, the saccharification of which has been initiated by the diastase of malt, were generally accepted, the difficulty of distinguishing analytically between the different classes of cereal vinegars would remain.

If prepared cereals are employed, the results will differ from those obtained with ordinary raw grain, as is shown by the following analyses of prepared grain, which have often been used in the manufacture of vinegar. These results are quoted by Nettleton †

The effect of the torrefying process on the barley is to reduce the oil and water, and to increase the proportion of starch, while leaving the amounts of mineral constituents and nitrogenous substances practically the same.

In the case of the flaked preparations similar changes take place, while the amounts of ash, nitrogenous sub-

\* *Garungstechnische Untersuchungs-methoden* (Bauer), p. 143

† *The Manufacture of Spirit*, p. 394

stances, and phosphoric acid are but little affected, after making allowance for the different proportions of water in the cereal before and after treatment

	Torrefied or Popped Barley	Flaked Maize	Flaked Maize "Cerealine"
	Per cent	Per cent	Per cent
Moisture, .	3.9	7.75	13.33
Oil, . . .	1.97		1.32
Albuminoids { Soluble,	0.88	0.65	} 8.54
{ Insoluble	12.62	7.75	
Starch and sugars, .	71.65	67.36	75.50
Woody fibre and cellulose,	6.03	15.25 (including the oil)	} 0.80
Mineral ash,	2.95	1.24	

Chapman \* has shown that the proportion of phosphoric acid in a vinegar depends, not only upon the composition of the cereal, but also upon the nature of the mineral salts in the brewing water

This was illustrated by the following experiments, in which two different malts were mashed with waters of different degrees of hardness, and the proportions of phosphoric acid in the filtrates were determined —

MALT, A	Phosphoric Acid ( $P_2O_5$ ) Grains per Gallon
Distilled water,	46.56
Water containing 20 grains total solids,	42.44
Very hard water,	30.44

MALT, B	
Distilled water,	44.77
Water containing 20 grains total solids,	37.61
Very hard water,	26.88

\* *Analyst*, 1912, xxxvii, 123.

In the case of vinegars brewed with very hard water Chapman found that almost the whole of the phosphoric acid was left in an insoluble condition (tribasic calcium phosphate) on ignition of the total solids

For these reasons he deprecates the fixing of an official standard for phosphoric acid in vinegar

In like manner, the proportion of nitrogen is influenced by the conditions of brewing. If low-dried malt and low mashing temperatures be used, the nitrogen will be higher than if high-dried malts are employed, or part of the wort be boiled after mashing, as is sometimes done to promote the final filtration of the vinegar. The addition of ferrocyanide as a clarifying agent (see p 131) precipitates proteins, and thus reduces the proportion of nitrogen, and these instances afford further illustrations of the dangers mentioned by Chapman (*loc cit*) "of setting up official standards for the composition of manufactured foodstuffs."

**Optical Standard.**—In 1906 malt vinegar was defined by the United States Department of Agriculture (Circular No 19) as "a product made by the alcoholic and subsequent acetous fermentations, without distillation, of an infusion of barley malt, or cereals whose starch has been converted by malt, is dextro-rotatory, and contains in 100 cubic centimetres (20° C) not less than 4 grammes of acetic acid, not less than 2 grammes of solids, and not less than two-tenths (0.2) gramme of ash, and the water-soluble ash from 100 c.c. of the vinegar contains not less than 9 milligrammes of phosphoric acid ( $P_2O_5$ ), and requires not less than 4 c.c. of  $\frac{N}{10}$  acid to neutralise its alkalinity."

It has been shown by Chapman\* that vinegar brewed from barley malt and cereals need not necessarily be dextro-rotatory, but that the proteins and their hydrolytic products may cause the vinegar to show a lævo-rotation. For example, practically the whole of a manufacturer's stock of vinegar showed a lævo-rotation of  $-0.56^{\circ}$  to  $-0.76^{\circ}$  when examined in a 200 mm tube, although no sugar had been used in the brewing.

**The Malt Vinegar Question.**—Few problems that have arisen in the administration of the Food and Drugs Acts have presented more difficulties than the question of what is or is not "malt vinegar," for there is no legal definition of the product, and all attempts to obtain a binding decision have hitherto proved fruitless.

As far back as 1894 the subject came into prominence in connection with certain vinegar prosecutions in the Midlands, and a Conference of the Society of Public Analysts† was held with the idea of obtaining some concerted agreement upon the point.

In the course of the discussion it soon became evident that there was a great divergence in the views held by leading Public Analysts on this subject. For example, while one speaker held that "malt vinegar" ought to be derived solely from malted barley, a second was prepared to pass a product brewed from a mixture of 10 per cent. of malt and 90 per cent. of barley, and a third remarked that "no one would doubt for a moment but that 'malt' was a term applied to a mixture of malt and barley only." Still greater latitude was allowed by another Public Analyst, who urged the Society to adopt the view that malt vinegar was "a product initiated by

\* *Analyst*, 1912, xxxvii., 123

† *Analyst*, 1894.

malt alone, raw grain may be used with it in the mash-tun, because the utilisation of its starch is absolutely restricted to the action of the malt, and therefore the constituents of the wort may be said to be strictly malt products." He would not admit "the products of starch hydrolysed by sulphuric acid or in other ways than by diastase"

The desirability of some agreement being reached, both in the interest of the profession and of the public, was pointed out by more than one speaker, while Mr. A. H. Allen remarked that he regretted that the vinegar manufacturer had sometimes been hardly dealt with by the Public Analyst

It was hardly surprising, however, in view of the divergency of opinions that the discussion should have ended without any definition of "malt vinegar" having been formulated by the Society

The result has been that individual Public Analysts when called upon to examine samples of malt vinegar have had to form their own definitions and fix their own standards, and conflicting decisions which settle nothing are constantly being given in the police courts all over the country.

For example, it was decided some years ago in the North of England that a vinegar manufactured from a mixture of malt and flaked maize was "malt vinegar," and costs were allowed against the county authorities, whereas in 1912 a Worcestershire bench held that flaked maize or maize grits ought not to be a constituent of malt vinegar, and fined the defendants

We have thus the farcical position that a man is regarded as an honest man for selling in one part of England

an article for the sale of which in another county he would be subjected to a criminal prosecution.

The want of some authoritative statement has been so keenly felt that in 1911 the Association of Vinegar Brewers requested the Local Government Board to fix a definition for malt vinegar. The Board replied (Dec. 15th, 1911), that they had no power to fix legal definitions for vinegar, but they suggested definitions that might be acceptable to all concerned in the manufacture and examination of vinegars, viz —

#### “GENERAL STANDARD FOR VINEGAR.

*Vinegar* is a liquid derived wholly from alcoholic and acetous fermentations; it shall not contain less than 4 grammes of acetic acid ( $\text{CH}_3 \cdot \text{COOH}$ ) in 100 cubic centimetres of vinegar, it shall not contain arsenic in amounts exceeding 0.0143 milligramme per 100 cubic centimetres of vinegar, nor any sulphuric or other mineral acid, lead or copper, nor shall it contain any foreign substance or colouring matter except caramel. *Malt vinegar* is derived wholly from malted barley or wholly from cereals, the starch of which has been saccharified by the diastase of malt.

#### “ARTIFICIAL VINEGAR.

*Artificial Vinegar* is any vinegar or substitute for vinegar containing or derived from any preparation containing any added acetic acid which is not wholly the product of alcoholic and subsequent acetous fer-



mentation It shall contain not less than 4 grammes of acetic acid ( $\text{CH}_3 \text{ COOH}$ ) in 100 cubic centimetres of the artificial vinegar It shall not contain arsenic in amounts exceeding 0.0143 milligramme per 100 cubic centimetres of vinegar, nor any sulphuric or other mineral acid, lead or copper, nor shall it contain any foreign substance or colouring matter except caramel "

It will be seen that this definition for malt vinegar restricts the use of the term to the products of the mash-tun, and excludes those made by the conversion process. It thus supports the view put forward by several public analysts that the term " malt " should refer to the agency by which the starch of the grain is hydrolysed

On the other hand, it permits the use of any cereal (including rice or maize), provided that sufficient malted grain is present to effect the hydrolysis

Unfortunately, this definition has not been generally accepted by Public Analysts, for since it appeared there have been several prosecutions for the sale of vinegars derived in part from products other than malt, and there has been the usual result of conflicting decisions by magisterial benches in different parts of the country It is to be hoped that before long this definition may be legalised by statute so as to put an end to the present state of uncertainty and confusion

The following analyses, made by the writer, show the characters of the products sold as malt vinegar by leading manufacturers, the samples having been bought at various times during the last twelve years —

## "MALT VINEGARS."

No	Specific Gravity at 15° C	Acetic Acid.	Total Solids	Ash.	Phosphorus Acid ( $P_2O_5$ )	Nitrogen	$P_2O_5$ on "Original Solids"		Nitrogen on "Original Solids"
							Per cent	Per cent	
I.	1017.5	5.1	2.74	0.49	0.076	0.07	0.69	0.64	0.64
II.	1021	5.4	3.84	0.39	0.13	0.14	1.08	1.23	1.23
III.	1015	5.1	2.2	0.46	0.07	0.09	0.75	0.90	0.90
IV.	1014.5	5.1	1.68	0.164	0.03	0.026	0.32	0.28	0.28
V.	1017.5	5.4	2.76	0.30	0.07	0.10	0.04	0.05	0.05
VI.	1017.5	5.9	2.78	0.36	0.11	0.10	0.94	0.86	0.86
VII.	1020	6.0	3.23	0.31	0.11	0.11	0.91	0.93	0.93
IX.	1013	4.5	1.75	0.24	0.09	0.08	1.00	0.90	0.90
X.	1017	5.1	2.4	0.49	0.08	0.09	0.85	0.94	0.94
XI.	1021.1	5.9	3.67	0.336	0.044	0.14	0.34	1.11	1.11
XII.	1011.5	4.4	1.5	0.31	0.017	0.0164	0.21	0.20	0.20
XIII.	1020	5.2	4.18	0.62	0.06	0.09	0.50	0.82	0.82
XIV.	1022	5.2	4.37	0.38	0.106	0.102	0.86	0.83	0.83
XV.	1013.5	5.1	2.1	0.19	0.04	0.035	0.41	0.37	0.37
XVI.	1014	4.3	2.04	0.47	0.075	0.062	0.83	0.70	0.70

Vinegars made by the same manufacturers as Nos IV., XII, and XV, and giving similar analytical results, have been made the subjects of prosecution, on the grounds of not being wholly malt products. The low nitrogen and phosphoric acid results were attributed by the defence to the use of cereals other than malted barley. In some cases there were acquittals and in others convictions.

The vinegar No XI. was remarkably high in nitrogen and abnormally low in phosphates, and for this reason the makers were prosecuted, but won their case. The explanation of the abnormal figures is that the vinegar was brewed from a mixture of green malt and rice, the former being responsible for the high nitrogen and the latter for the low phosphoric acid.

Several of the vinegars included in the above table were admittedly manufactured by the conversion process. No XVI was a typical instance, and it was characterised by a high percentage of mineral matter, in which, too, there was a large proportion of sulphate.

The low proportion of total solids in No IX. is unusual, and has on more than one occasion been the subject of comment. It could be satisfactorily accounted for by the fermentation having been carried to a lower point than is usually the case.

### CIDER VINEGAR.

Very little cider vinegar is manufactured in this country, but in the United States it is in much greater demand than either wine or malt vinegar.

Analyses of twenty-two typical samples of various

origin were published by Leach and Lythgoe,\* and from their results they suggest that certain chemical standards should be fixed. Thus, in their opinion, pure cider vinegar should contain at least 4.5 per cent. of acetic acid and 2 per cent. of ash (which should be at least 6 per cent. of the total solids, and have an alkalinity equivalent to at least 65 c.c.  $\frac{N}{10}$  acid per 1 gram). Not less than 50 per cent. of the phosphates should be soluble in water. The reducing sugars should not vary in amount after inversion, and should not exceed 25 per cent. of the total solids. The specific rotation of the clarified vinegar should be between  $-0.1^\circ$  and  $-4.0^\circ$  Ventske (200 mm. tube). The presence of malic acid should be ascertained by the lead acetate and calcium chloride tests (see p. 154).

In the opinion of Tolman and Goodnow,† the older analyses of cider vinegar are not applicable to the vinegars which are now being made by the "quick" process. Their experiments indicated that the loss in volume during acetification was so small that it was possible, without correction, to compare the results with those given by the original cider. This contained on the average 7.7 per cent. by volume of alcohol and 0.27 per cent. of acetic acid, and yielded a vinegar containing 5.77 per cent. of acetic acid and 0.4 per cent. of alcohol, the loss of alcohol during acetification being thus over 20 per cent.

The total solids, ash, and glycerin were but little affected by acetification, while the non-sugars were substantially the same in the cider and the vinegar. Aldehydic compounds were formed, and it was necessary to

\* *J. Amer. Chem. Soc.*, 1904, **xvii**, 375

† *J. Ind. Eng. Chem.*, 1913, **v**, 928

evaporate the vinegar repeatedly to expel these, otherwise the sugars were overestimated by Fehling's solution by 0.15 to 0.2 gram per 100 c.c.

The fixed acids were greatly reduced by acetification, and fell as low as 0.04 per cent (as malic acid), on the other hand, the pentosans increased by about 50 per cent.

The following analysis of a French cider vinegar is given by Calvet\*.—Total acidity as acetic acid, 4.71, fixed acidity (as  $\text{H}_2\text{SO}_4$ ), 0.19; total solids, 1.98, reducing sugars (as dextrose), 0.27, ash, 0.26, and alcohol, 0.7 per cent.

## WINE VINEGAR

Wine vinegar is the predominating product of France, just as malt vinegar is in this country, and cider vinegar in the United States. Red or white wines are used in the manufacture, and the resulting vinegars accordingly vary in colour.

As a rule, the acetic strength is considerably higher than in the case of malt vinegar, and is usually not less than 7 or 8 per cent. The specific gravity is low, owing to the small amount of solid matter present.

An analysis made by the writer of one of the principal French wine vinegars sold in this country gave the following results.—Specific gravity, 1.017, acetic acid, 7.2, total solids, 1.7, ash, 0.25, phosphoric acid, 0.042; and nitrogen, 0.013 per cent.

Vinegars made from British wines contain more total solids than French wine vinegars, and these are of a more

\* *Loc cit*, p. 61.

viscous character from the presence of the sugar in the wine

The distinguishing characteristics of genuine grape wine vinegars are the presence of tartaric acid and inositol, for the detection of which see pp. 155, 153

The following results were obtained in the analysis of white wine vinegars by the Municipal Laboratory of Paris —

	Specific Gravity	Total Solids	Sugar	Potassium Bitartrate	Ash	Acetic Acid
		Per cent	Per cent	Per cent	Per cent	Per cent
Maximum,	1 0213	3 19	0 46	0 36	0 69	7 38
Minimum,	1 0129	1 38	0 56	0 07	0 16	4 44
Mean,	1 0175	1 93	0 22	0 17	0 32	6 55

The presence of glucose vinegar in wine vinegar may be detected, according to Delluc,\* by the fact that in the former the ratio of  $\frac{\text{extract}}{\text{dextrose}}$  approximates to unity. This is shown by the following analyses of white and red vinegars made from coloured glucose syrups. —

	White Vinegar	Red Vinegar
Specific gravity at 15° C.,	1-025	1-012
Acetic acid, per cent ,	6 65	4 20
Total solids, per cent ,	2 41	1 12
Reducing sugars, as dextrose,	2 26	0 98
Ratio, $\frac{\text{total solids}}{\text{dextrose}}$ ,	1-06	1 14

For the method of determining reducing sugars, see p. 152.

\* Calvet, *loc cit.*, p 61

Wine vinegars are frequently adulterated in France with spirit vinegar, or, rather, the vinegar is prepared by acetifying a mixture of wine and dilute alcohol

Distilled wine vinegar is made by distilling either red or white wine vinegar under reduced pressure (see p 135) It is commonly sold under the name of *white wine vinegar*, and this name is also wrongly applied to distilled malt vinegar

### WHEY VINEGAR

This is made from the whey of milk fortified with sufficient sugar to give the alcohol necessary for the production of the acetic acid

A sample examined by Filaudeau and Vitoux\* had the following characters —Specific gravity at 15° C, 1 0184, total acidity as acetic acid, 6 51, fixed acidity as lactic acid, 0 18, total solids, 2 10, reducing sugars, as lactose, 1 44, nitrogenous substances as casein, 0 17, ash, 0 14, sodium chloride, 0 09, and insoluble ash (tribasic calcium phosphate), 0 11 per cent

### FRUIT AND HERB VINEGARS

Vinegar may be made from any fruit containing sufficient sugar for the production of the necessary alcohol

In other cases—*e g*, raspberry vinegar—the vinegar is made by steeping the fruit in distilled vinegar and sweetening the product with cane sugar

A similar process is employed in preparing tarragon and other products of the same nature, the herbs being

\* *Ann des Falsificat*, 1909, II, 208

steeped in a brewed or distilled vinegar to impart the necessary flavour

### DATE VINEGAR

A few years ago a spirited attempt was made in this country to create a demand for date vinegar in place of malt vinegar. The products put upon the market had a characteristic flavour and aroma, somewhat recalling that of a wine vinegar.

Compared with a normal barley malt vinegar, they were low in nitrogen and phosphoric acid. Three commercial samples examined by the writer in different years gave the following percentage results —

	Acetic Acid	Total Solids	Ash	Phosphoric Acid	Nitrogen
I	5.0	2.61	0.48	0.051	0.031
II.	5.34	2.80	0.49	0.052	0.024
III.	5.8	2.47	0.49	0.038	0.030

In spite of much advertising, date vinegar never became a serious competitor of malt vinegar, and of late years appears to have disappeared from the market.

### SPIRIT VINEGARS.

The manufacture of vinegar from dilute alcohol has become a serious competitor of the old-established industry of wine vinegar in France, since the product can be sold at a much lower price.

Spirit vinegar is usually coloured with a little caramel, to make it resemble wine vinegar more closely. Its odour is much more pungent, and lacks the bouquet



of the wine product It contains much less solid matter and ash than wine vinegar, but differs from dilute acetic acid in containing alcohol, aldehyde, and tartaric acid

The following analysis shows the composition of a typical French product —Total acidity as acetic acid, 7.68, fixed acidity (as  $\text{H}_2\text{SO}_4$ ), 0.03, total solids, 0.22, tartaric acid, 0.08, and ash, 0.04 per cent, ratio  $\frac{\text{extract}}{\text{dextrose}}$ , 34.9

**Essigsprit or Vinegar Essence.**—A German product is prepared from potato spirit by a fermentation process. It usually contains about 11 to 12 per cent of acetic acid, and has a slight yellow tint, and an agreeable aromatic odour Until recently, it was imported into this country in large quantities, and used for pickling purposes as a cheap substitute for malt vinegar

A typical sample examined by the writer had the following characteristics —Acetic acid, 12.3, total solids, 0.16, and ash, 0.02 per cent

A concentrated acetic acid is also made by neutralising the *Essigsprit* with lime and distilling the calcium acetate with sulphuric acid *Spirit acid* thus prepared has a much more pleasant aroma, and contains fewer impurities than much of the wood acetic acid imported into England

## WOOD VINEGAR

Wood vinegar, as its name denotes, is nothing more than dilute acetic acid, coloured with caramel, and sometimes flavoured by the addition of a small quantity of brewed vinegar

It has a pungent odour of acetic acid, and lacks the

aroma of malt vinegar, although it is frequently fraudulently sold under the name of 'malt vinegar'

The following analyses of commercial samples of artificial vinegar were made by the writer during the last ten years —

## COMPOSITION OF ARTIFICIAL VINEGARS.

Sold as	Specific Gravity at 155° C	Acetic Acid	Total Solids	Ash	Phos phoric Acid	Nitrogen	Colour Lovi bond "52" Series
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	
"Wood vinegar,"	1.009	4.9	0.52	0.03	0.02	0.009	24
"Pale malt vinegar,"	.	5.2	0.18	0.018	trace	0.008	15
"Double re-fined malt vinegar,"	1.006	4.4	0.60	0.036	0.005	none	
"Malt vinegar,"	.	4.25	0.65	0.24	trace	trace	

In the case of the "double refined malt vinegar," the whole of the colouring matter could be precipitated by fuller's earth, but this was not possible with the last sample. It was, therefore, probable that in the latter vinegar some of the colour was derived from the addition of grain vinegar as a flavouring agent.

The traces of phosphoric acid and nitrogen were probably present in the caramel used for colouring these products. The high ash of the last sample was due to the presence of 0.18 per cent of common salt.

Artificial vinegars usually contain at least 4 per cent of acetic acid, and there have been numerous prosecutions for the sale of products of lower acidity (see p. 172).

## APPENDIX I

## IMPORT DUTIES ON VINEGAR AND ACETIC ACID.

## British India—

Vinegar in casks,	2½ per cent <i>ad valorem</i> .
Vinegar not in casks	5       ,       ,,

## Ceylon—

Vinegar in casks,	2½       ,,       ,
Vinegar not in casks,	5½       ,       ,,

## Mauritius—

Vinegar not exceeding 8 degrees by Salleron's acétimètre,	per gall	Rs 0 7 <sup>8</sup> / <sub>11</sub> cts
(With an additional duty of <sup>8</sup> / <sub>11</sub> cts for every degree above 8 degrees by Salleron's acétimètre )*		

Seychelles,	12½ per cent <i>ad valorem</i>
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## Australia—

Vinegar, vinegar essence, and acetic acid vinegar (standard as prescribed by Departmental Bye-laws), the product of malt, grain, or fruit juice by alcoholic and acetic fermenta- tion, containing not more than 6 per cent of absolute acetic acid,	per gall	£0 0 6
Vinegar not the product of malt, grain, or fruit juice, per gall		0 2 0
Solutions containing more than 6 per cent, but less than 30 per cent,	per gall	0 3 9
For every 10 per cent additional,	„	0 1 3

## Papua—

All kinds,	per gall	0 0 6
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\* See p 138

## New Zealand—

Vinegar not exceeding 6.5 per cent of acidity as acetic acid,	per gall	0	0	6
Otherwise,	"	0	0	7½
Acetic acid up to 30 per cent strength,	per lb	0	0	1½
For every 10 per cent additional acidity,	"	0	0	0½
Fiji,	per gall	0	0	6

## British South Africa—

## Glacial acetic acid—

- (1) In bottles, etc., not exceeding an imperial quart—  
 Under British preferential tariff, per gall £1 4 6  
 Under general tariff, " 1 12 5
- (2) In larger quantities—  
 British preferential tariff, " 1 4 0  
 General tariff, " 1 11 11

## Vinegar, vinegar essence, acetic (other than glacial) and pyroigneous acids, not exceeding proof strength—

- (1) In bottles, etc., not exceeding 1 quart—  
 British preferential tariff, £0 1 0  
 General tariff, 0 1 1
- (2) In larger quantities—  
 British preferential tariff, 0 0 6  
 General tariff, 0 0 7

And in addition in either case for each degree of strength in excess of proof—

- Under British preferential tariff, per degree £0 0 3  
 Under general tariff, " 0 0 4

(Note—"Proof" will be held to be equal to 6 per cent of absolute acetic acid, and shall be determined in the manner prescribed by the Customs. In *Cape of Good Hope*, the sale is prohibited of vinegar to which have been added ingredients injurious to health, and which does not contain at least 3½ per cent. of absolute acetic acid (Act No 19 of 1908).)

Nyasaland Protectorate,	10 per cent	<i>ad valorem</i> .
Uganda Protectorate,	10	" "
British East Africa,	10	" "
Somaliland—		
Imported in Zeyla,	5	" "
Imported in other ports,	7	" "
		13

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Nigeria, 10 per cent *ad valorem*

## Gold Coast—

Imported west of the Volta, 10 „ „  
Imported east of the Volta, 4 „ „

Sierra Leone, 10 „ „

Gambia, 5 „ „

## Canada—

Vinegar and acetic acid (not exceeding proof strength—

Under British preferential tariff, per gall £0 0 4 93

Under intermediate tariff, „ 0 0 6 17

Under general tariff, „ 0 0 7 40

With additional duties of 0 74d, 0 86d, and 0 99d for each  
degree under proof

(The strength of proof shall be held to equal 6 per cent of absolute acetic acid, and shall be determined in the manner prescribed by the Governor-in Council )

## Newfoundland—

In cask, per gall £0 0 7 40

In bottle, 30 per cent *ad valorem*

Bahamas, 20 „ „

Jamaica, 16½ „ „

St Lucia, per gall £0 0 4

St Vincent, 10 per cent *ad valorem*

Barbados, 10 „ „

Grenada, 10 „ „

Virgin Islands, per gall £0 0 3

St. Christopher, „ 0 0 4

Antigua, „ 0 0 4

Montserrat, „ 0 0 4

Dominica, „ 0 0 3

## Trinidad and Tobago—

Acetic acid below 6 per cent strength, per gall £0 0 6

Acetic acid above 6 per cent strength, „ 0 2 6

Vinegar, „ 0 0 6

**Bermuda—**

All kinds,	10 per cent <i>ad valorem</i>
------------	-------------------------------

**British Honduras—**

All kinds,	12½ „ „
------------	---------

**British Guiana—**

Vinegar, containing less than 10 per cent. of acetic acid,	
per gall.	£0 0 5

**Malta—**

Per barrel of 9½ gallons,	0 2 0
---------------------------	-------

**Cyprus—**

All kinds,	8 per cent <i>ad valorem</i>
------------	------------------------------

No import duties are charged in the following countries —

Aden, Straits Settlements, Hong-Kong, Falkland Islands, N E.  
Rhodesia, St Helena, and Gibraltar

## APPENDIX II

## FRENCH DUTIES ON VINEGAR.

PRIOR to the year 1872 the only vinegar upon which duty was charged in France was that made from beer, the raw materials for which were taxed in accordance with a law of 1816. The duty levied in 1872 upon alcohol intended for the manufacture of spirit vinegar led to complaints from the vinegar makers of the unfair advantage given to the manufacturers of wine vinegar, with the result that in 1875 a uniform tax was imposed upon vinegar of every description in accordance with the following tariff. The strength of the vinegar is based upon the results obtained with Salleron's acetimetre (p 138)

## FRENCH DUTIES ON MANUFACTURED OR IMPORTED VINEGAR

	Francs	
1 Vinegars containing 8 per cent or less acetic acid,	5	} per hecto- litre
"      "      9 to 12 per cent acetic acid,	7 50	
"      "      13 to 16 per cent acetic acid,	10	
2 Acetic acids and vinegars containing 17 to 30 per cent acetic acid,	18 75	
Acetic acids and vinegars containing 31 to 40 per cent acetic acid,	25	
Acetic acids and vinegars containing more than 40 per cent acetic acid,	52 52	
3. Glacial acetic acid in the solid condition	62 50 per 100 kilos	

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